Defects in Crystalline Solids (Part-I)
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Lecture - 04
Vacancy Concentration Measurement Techniques

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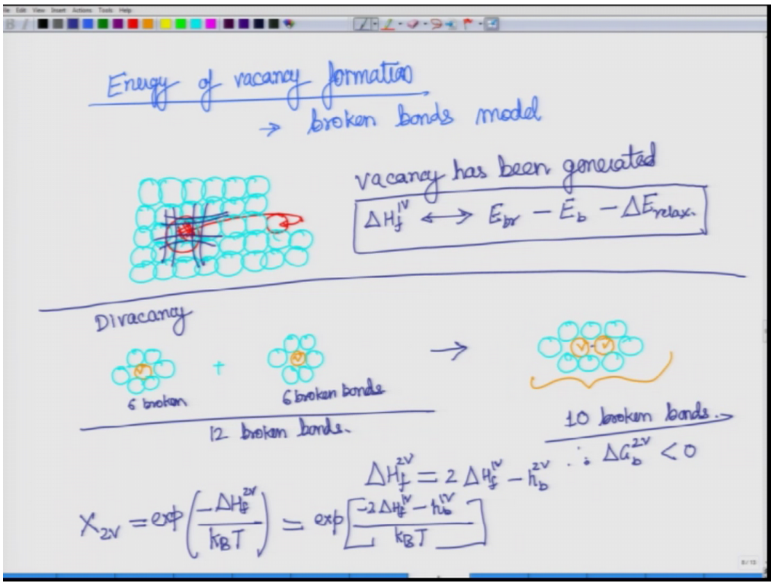

Energy of vacancy formation

→ broken bonds model

vacancy has been generated

$\boxed{\Delta H_f^{1V} \leftrightarrow E_{br} - E_b - \Delta E_{relax}}$

Divacancy

6 broken + 6 broken bonds →

12 broken bonds.

10 broken bonds →

$\therefore \Delta G_b^{2V} < 0$

$\Delta H_f^{2V} = 2\Delta H_f^{1V} - h_b^{2V}$

$X_{2V} = \exp\left(\frac{-\Delta H_f^{2V}}{k_B T}\right) = \exp\left[\frac{-2\Delta H_f^{1V} - h_b^{1V}}{k_B T}\right]$

So, as I showed you in a previous lecture, this is divacancy formation equation or reaction. So, there is one vacancy here somewhere isolated another vacancy over here isolated with a 6 broken bonds over here, it has 6 broken bonds here and let say by a reaction it forms a divacancy. So, the there is a bonding between these 2.

Now, here we see there is you needed 12 broken bonds. So, the energy required is proportional to 12 E b r, here, we have 10 broken bonds. So, there are only 10 it is proportional to 10 E b r which means that for this relation for this reaction, we should have delta G bonding of 2 vacancies less than 0 meaning, it should be a desirable reaction it should energy is getting reduced. So, this is the system energy enthalpy is getting reduced and therefore, this reaction should proceed forward.

Now, let us see how much how many of these bonds what will be the concentration of this dibonds or divacancies. So, what is the delta H f like I said earlier that will not go through the whole derivation we will now look only at the formation energy we know the if we can find out the formation energy in this case, it will be equal to 2 do 2 delta H f one v this is not that not that right equation because as we know that this should have a lower energy. Therefore, there is some term which must be reducing it and that term is the bonding between these two. So, this is let us denote this by h underscore h subscript v and superscript 2 v to denote that it is a divacancy. So, there is a bonding between these 2 vacancies and this is denoted by h under subscript b, superscript 2 v and this is the reducing term. So, the total delta h f 2 v is as you can see is less than 2 times delta H f 1 v.

And once we have this we can write the equation as let me write it here X 2 v equal to exp this is without the formation entropy term. So, this is again the condensed form of the equation you can always go back and expand those things now that you know the methodology to do that ok. So, this is the equilibrium concentration of divacancies.

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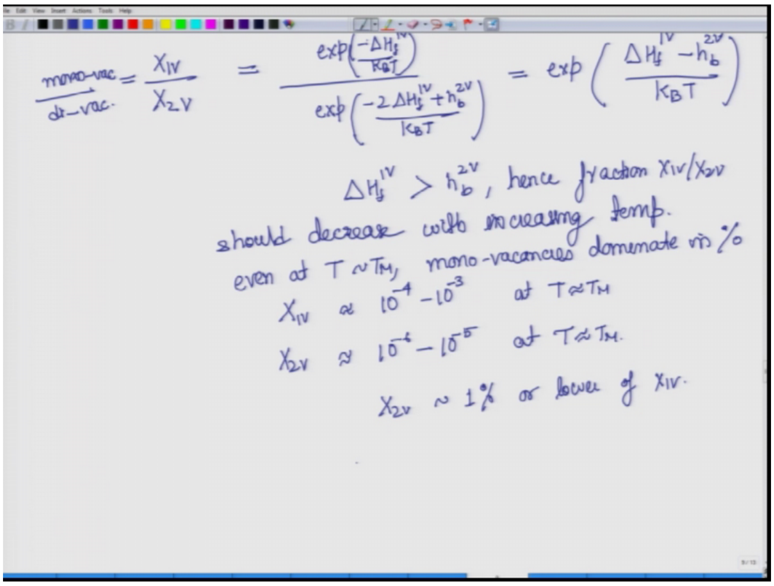

$$\frac{\text{mono-vac}}{\text{di-vac.}} = \frac{X_{1V}}{X_{2V}} = \frac{\exp\left(\frac{-\Delta H_f^{1V}}{K_BT}\right)}{\exp\left(-\frac{2\Delta H_f^{1V} + h_b^{2V}}{K_BT}\right)} = \exp\left(\frac{\Delta H_f^{1V} - h_b^{2V}}{K_BT}\right)$$

$\Delta H_f^{1V} > h_b^{2V}$, hence fraction X_{1V}/X_{2V} should decrease with increasing temp.

even at $T \sim T_M$, mono-vacancies dominate in %

$X_{1V} \approx 10^{-4} - 10^{-3}$ at $T \approx T_M$

$X_{2V} \approx 10^{-6} - 10^{-5}$ at $T \approx T_M$.

$X_{2V} \sim 1\%$ or lower of X_{1V}.

Now, let me go back and so, try to find what will be the ratio of X 1 v by X 2 v, it is not very difficult I have given you both the relation you have to simply divide it what was the X 1 v X 1 v is equal to exp minus delta H f let me there is not enough space. So, let me rewrite it by K B T and for X 2 v we have again expressing it in terms of single vacancies formation energy which is delta H f 1 v plus hb 2 v by K B T. Now since these are exponential terms and we are dividing it. So, it is as could as subtracting the term inside exponential over here this term will sub to get subtracted from the one on the numerator.

So, this becomes. So, this is the ratio of monovacancies to divacancies as you mean the system is in thermodynamic stable state mono vacancy by divacancy. Now what do we see here? Obviously, this term which is delta H f 1 v is greater it would be greater by a big margin than this term h b 2 v. Hence the fraction this fraction that we have talked about hence fraction X 1 v by X 2 v should decrease with increasing temperature meaning as you become as you keep changing the temperature the number of divacancies should increase the proportion of the divacancy should increase with respect to monovacancies.

However, you must be careful that even at temperature as close to tm even at T approximately equal to tm the proportion may have increased with respect to room temperature or lower temperature, but it still it is mostly the it is the monovacancy that dominate. So, it is monovacancies dominate in percentage to give you a rough idea X 1 v would be approximately of the order of 10 to the power minus to 10 to the power minus 3 at T, approximately just little less than tm because here not going into the liquid state and monovacancies concentration would be of the order of 10 to the power minus X to 10 to the power minus f 5 at T approximately equal to t.

What does this say this says that X 2 v would be approximately one percent or lower of X 1 v. So, you can see that is still it is the monovacancies that will dominate it is not that divacancies the fraction is decreasing. So, divacancies do not start dominate it is still of large fraction of monovacancies that is present in the system ok.

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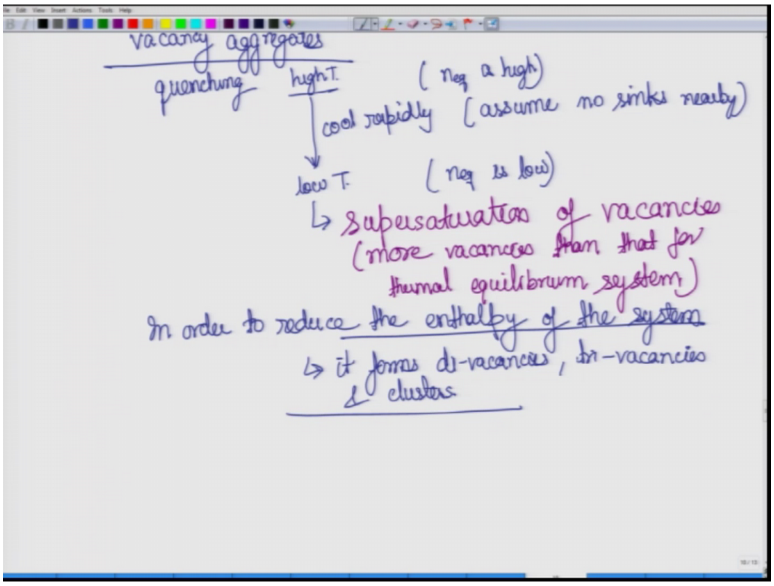

vacancy aggregates

quenching high T. (n_{eq} a high)

cool rapidly (assume no sinks nearby)

low T. (n_{eq} is low)

↳ supersaturation of vacancies (more vacancies than that for thermal equilibrium system)

In order to reduce the enthalpy of the system

↳ it forms di-vacancies, tri-vacancies & clusters

So, now let us get to now that we have seen monovacancies divacancies. Now let us talk about vacancy aggregates let say that you are using some non equilibrium process like quenching. So, what happens in quenching somewhere at a very high temperature? So, high temperature you cool it rapidly to low temperature that is quenching. So, over here the equilibrium concentration which is n equilibrium is high here n equilibrium should be low.

But since you are cooling rapidly and the mobility of vacancies is not very large that they can diffuse out to the nearby sink and we can assume that there will be in for most of them there will not be sink very close by available what is a sink will come to that in a moment. So, things for the time being we can assume that the sinks are the place where vacancies can go and merge where they will disappear. So, we here we can assume that no sinks nearby. So, just like sinks there will also be sources from where if there is a place where vacancies can disappear. So, there can also be a place where vacancies can appear in a we are talking about a real system real material. So, assume no sinks nearby.

So, what will happen that that lower temperature, you will have at this temperature you will have super saturation of vacancies meaning more vacancies than is allowed by thermodynamics or more than what would be expected for a thermally equilibrium system.

Now, here what happens is that in order to reduce the fraction of monovacancies, what the system does to reduce the energy because if there are lots of monovacancies the enthalpy is very high for the system. So, in order to reduce the energy of the system how would the system reduce the monovacancies it forms you guessed it try it forms divacancies tri vacancies and clusters

So, when you have divacancies and tri vacancies as I showed you earlier that when they form they come together, then they will have lower energy than independent vacancies and therefore, the energy of the system gets reduced. So, that way you will have you the system will be able to reduce the enthalpy or the overall energy of the system.

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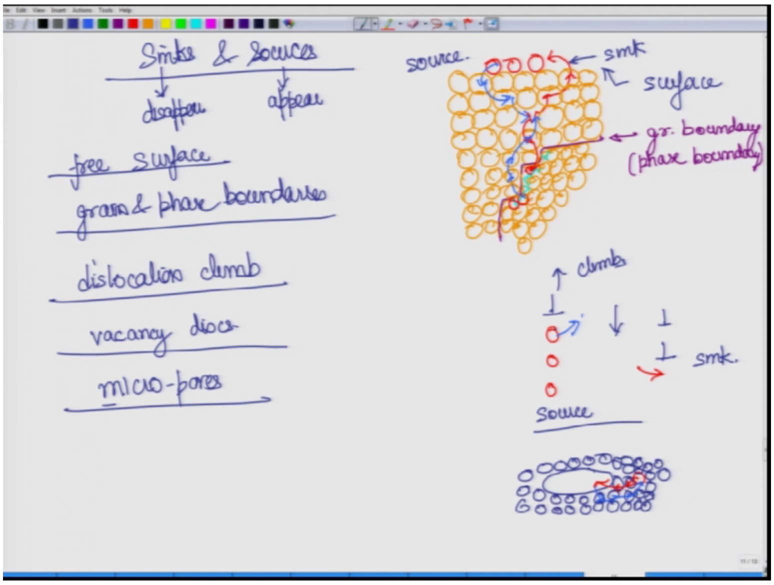

Sinks & Sources

disappear

appear

free surface

grain & phase boundaries

dislocation climb

vacancy discs

micro-pores

So, now coming to the point that I talked earlier sinks and sources inside a material, we are talking about increasing in the vacancy concentration with increasing temperature or reducing of the vacancy concentration with reducing temperature. So, where do they appear where do they disappear from. So, these are the places where they appear from are called sources and the places where they disappear are called sinks.

Now, here you may think these are some strange phenomena, but it is not like that or not some very out of the world features what we have are some simple components the structural components of a material like surface now what will happen how it can a surface generator allow the formation or the. So, as act as the sink and source let us see. So, let say this is a material and like I said. So, let say I have this, I let this be a vacancy and this is the simple 2 dimensional system that I am drawing here. So, here is your vacancy.

Now, because vacancies can diffuse; so, this vacancy can hopt to this place this hopt to this place and once it is here, then it is on the surface and surface has already surface is already uneven and even it can move to somewhere on the completely outside surface. So, it is as good as saying that we have vacancies over here vacancies over here or and vacancies or here. So, this way this vacancy has disappeared onto the surface or the other way around this vacancy can hop into here although this particular atom can move over here and this vacancy can move over here then it can move to here this then this can move to here.

So, in this case the surface acted like in this particular case it acted like a sink in the second case it acted like a source and which is actually the case for most of these structural units are the or the source and sinks most of them are act both as a source and also as a sink. So, this is a surface. So, surface is one example free surface.

Now, similarly we have grain and phase boundaries from your fundamental background in materials you would know that there are regions with extended crystallinity and they get interrupted by a region or a plane, which is called grain boundaries and we have more than one phases then it this will be called a phase boundary. So, in this same drawing that I have shown you here let me say that there is so onto the other side. So, this on this side you have let say the structure is very much or that will orientation is very much. So, like that, but on this side let say orientation is like this.

So, what we have here is this is a grain boundary if it where between 2 different phases then in that case it would be a phase boundary. So, the great difference between grain boundary and phase boundary is primarily that one of them is differentiating or is a partition between orientation 2 orientation of 2 different materials or 2 different phases or of same phases. So, that way grain boundary is also called homo phase boundary meaning both the phases on both the sites are same and a phase boundary is called a hetero phase or the hetero phase boundary because on the 2 sides of the interface boundary they are different phases.

So, from this point of view, there is not much difference what we have what we are particularly interested in is that when you have a boundary like this; what you see over here is that there are lots of empty phases. Now these empty phases what do these; what does that mean is that it is a potential site for vacancies to set or vacancies to come out and get into the system.

So, just like I showed you over here these vacancies can actually some from somewhere, let us say this is the vacancy it can hop from here and over to here. So, it acts like a sink or in the other case it can go from here to here and it will act like a source. So, this particular region where there is extra volume this free more free volume this can act as both as a source and a sink. So, that is another region or another structure which allows for formation and degeneration of vacancies.

Still another one is dislocation climb. So, we have a dislocation like this in a system and I am not drawing the system around it. So, when it climbs it moves up what happens is that it leads a trail of vacancies when it is climbing up when it is moving down then it absorbs these vacancies. So, this and there atoms come in till this place and there is absorption of vacancies. So, let say this is moving over here. So, whatever vacancies were in this particular region they get formation of vacancies and this is sink of vacancies. So, whatever vacancies are there it gets into this region and it gets consumed. So, this as acting like a when it is moving down, then it this acts like a sink and when it is moving up it acts like a source. So, this is another source or another way that this vacancies are generated or consumed.

Still another one is vacancy discs. So, inside a material you can have a disc made out of basically empty atoms. So, there is a region where there are no more atoms its. So, around it is still all atoms I am not trying to draw it here just trying to give you a rough scheme of things it is difficult to draw it here it is just that there is missing atom over here. So, this is like a vacancy disc.

So, now the again if there are some vacancies now. So, I have almost drawn it I thought I would not be able to draw ok. So, here the vacancy can move from here to here and over here. So, this is this becomes like a sink on the other hand because there is a vacancy there is a large region it can move on from here to here and here and then it will becomes a source. So, again vacancy discs can become a source and sink.

Similar to the vacancy discs if this is a little larger then you would call it micropores and so, this micropores which will act very similar to this can also act as source and sinks. So, now, we have looked at the various places from where vacancies may appear and where they may disappear.

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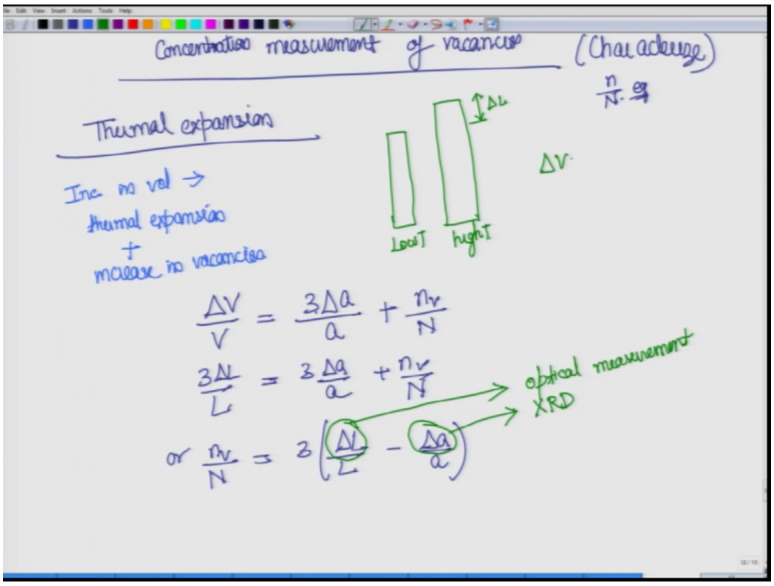

Concentration measurement of vacancies (Characterize)

$\frac{n}{N}$. eq

Thermal expansion

Inc in vol →
thermal expansion
+
increase in vacancies

$$\frac{\Delta V}{V} = \frac{3\Delta a}{a} + \frac{n_v}{N}$$

$$\frac{3\Delta L}{L} = 3\frac{\Delta a}{a} + \frac{n_v}{N}$$

$$\text{or } \frac{n_v}{N} = 3\left(\frac{\Delta L}{L} - \frac{\Delta a}{a}\right)$$

optical measurement
XRD

Now, let us look at another aspect with relation in respect to vacancies which is concentration measurement of vacancies. So, what we are trying to do here is characterize n by n and assuming that it is being done in a thermally stable process in a thermally in thermal equilibrium then what we get is a equilibrium fraction.

First method that we will discuss here is thermal expansion here let say we take a rod and we heat it. So, let us say it is at low temperature and this is at higher temperature. So, there will; obviously, be a increased in the length. So, there is a delta L actually what will what would change is delta v. So, the volume has increased

Now, this increase in volume can be attributed to 2 different aspects one is the thermal expansion meaning you lattice parameter has increased and another is because of increase in vacancies. So, we can put it put this equation like this, this is the total increase delta V by V. Now the thermal expansion which is because of the increase in the lattice parameter. So, lattice parameter is one dimensional. So, in order to consider to understand its affecting 3 dimension we will have to multiply by 3 which is approximate for the change in volume because of thermal expansion delta a by a and then nv by n which is anyways the 3 dimensional. So, we do not need to multiply any factor over here.

Now, this delta v by v can be written as 3 delta L by L equal to 3 delta a by a plus n v by or in other words from here, we can see that this relation becomes 3 delta L by L minus delta a by a. Now this relation is giving us the concentration of vacancies from whatever temperature to temperature you have calculated the delta L and for that you also need to know calculate the delta a. So, we need to measure these 2 quantities delta L and delta a how can you do delta L? Simple optical measurement like a camera which is watching the increase in the length because we have taken a rod so, optical measurement can give you what will be the delta L for delta a it is the lattice parameter and one of the best techniques to change to measure the change in the lattice parameter is X ray diffraction.

So, using these 2 techniques you can find delta L delta a and therefore, you will be able to find the change in the concentration of vacancies or the total increase in the volume because of vacancies.

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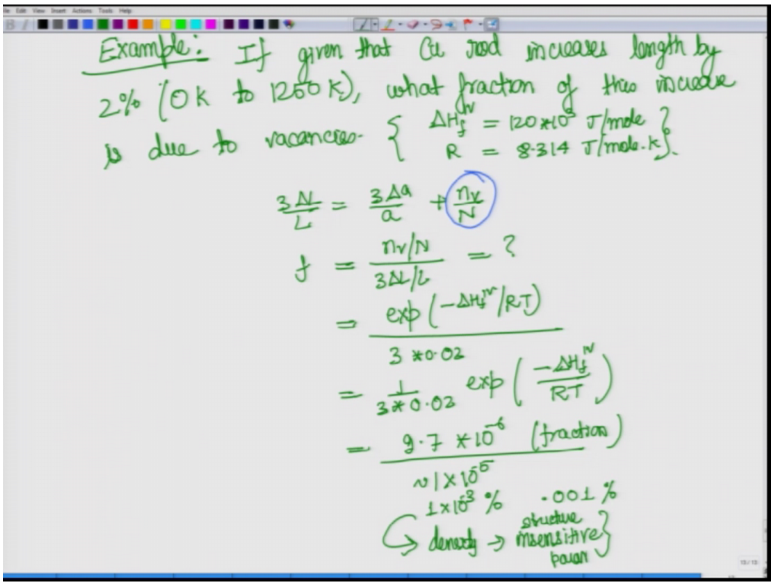

Example: If given that Cu rod increases length by 2% (0 K to 1250 K), what fraction of this increase is due to vacancies. $\left\{ \begin{array}{l} \Delta H_f^v = 120\times10^3 \text{ J/mole} \\ R = 8.314 \text{ J/mole.K} \end{array} \right\}$.

$$\frac{3\Delta L}{L} = \frac{3\Delta a}{a} + \frac{n_v}{N}$$

$$f = \frac{n_v/N}{3\Delta L/L} = ?$$

$$= \frac{\exp(-\Delta H_f^v/RT)}{3 * 0.02}$$

$$= \frac{1}{3 * 0.02} \exp\left(\frac{-\Delta H_f^v}{RT}\right)$$

$$= \underline{9.7 \times 10^{-6}} \text{ (fraction)}$$

$\sim 1 \times 10^{-5}$

1×10^{-3} % .001 %

density → {structure insensitive param}

Now with respect to that let us look at one example, it is given that copper rod increases by 2 percent length. So, increases length by 2 percent when heated from 0 Kelvin to 1250 Kelvin. What fraction now the question is what fraction of this increase is due to vacancies? What you are given is again the thermodynamic quantities delta H f 1 v is equal to 120; now here it is given in to given in joules per mole and for that corresponding R can be taken as 8.314 joule per mole per Kelvin.

So, what you understand about the question? We already know something from earlier equation which was that the total change in length which is 3 delta L by L is equal to 3 delta a by a plus nv by N, but what we are being asked is a fraction which is this. So, the question is what is this fraction of the total change.

So, what you have to find is f equal what means this f value which is nf nv by N by 3 delta L by L. So, this is what you need to find ok. So, here nv by N is very simple we have we just need to use the equation and since we are only given delta hf. So, we can ignore the entropy term. So, this is minus delta H f 1 v by RT like I said and 3 delta L by L. So, this is given 2 percent. So, delta L by L becomes 0.02. So, this is 1 over 3 into 0, let me correct this one exp minus delta H f 1 v by RT.

Now, if you solve it, you would see that you are getting something like this and I as you to solve these problems that example problems because these will form the basis of some of the assignments and maybe even final example. So, if you are able to solve this then you can you would feel comfortable solving those questions. So, this is a fraction.

So, the fraction would come out to one over 3 by one over 3 times 0.02 the whole of this fraction has to be multiplied by this exponential term and when you solve it you would get approximately nine point seven into 10 to the power minus 6 and we are talking about fraction. So, it is a approximately equal to 1 in to 10 to the power minus five or in other words, 1 into 10 to the power minus 3 percent which is how much 0.001 percent. So, of the total increase in the length of this copper rod when you go from 0 Kelvin to 1250 Kelvin, only 0.001 percent can be attributed 2 vacancies.

Now, this is what we can relate back to when we said that density is a insensitive parameter structure insensitive because you can see that even very close to melting point you are not contributing much to the volume which means the density would really not change because of the equilibrium concentration of vacancies.

So, this is this is giving you this example serve 2 purpose it helps you understand how this method of thermal expansion can be used to find nv by N and it is also giving you understanding that this total contribution of nv by N to the expansion is a very minuscule quantity and therefore, we can term density as a structure insensitive parameter. So, we will come back in a next lecture with few more techniques to measure vacancy concentration.

Thanks.