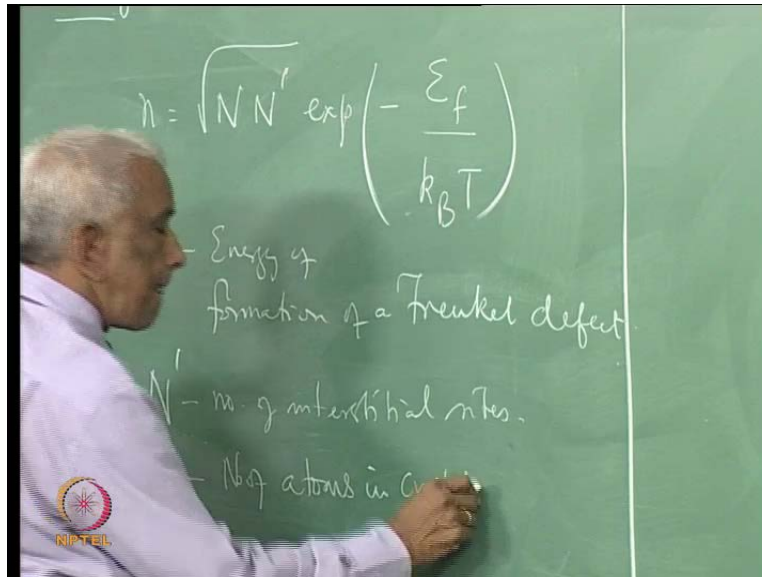


**Condensed Matter Physics**  
**Prof. G. Rangarajan**  
**Department of Physics**  
**Indian Institute of Technology, Madras**

**Lecture – 38**  
**Point Defects in Solids – Worked Examples**

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Today we are going to work some problems on the topic of point defects in solids.

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**Worked Example 91**

**Problem**

Show that the number of Frenkel defects in a crystal of  $N$  atoms is given by

$$n = \sqrt{NN'} e^{\frac{-E_f}{k_B T}}$$

where  $E_f$  is the energy of formation of the Frenkel defect and  $N'$  is the number of interstitial sites in the crystal.

The NPTEL logo is visible in the bottom left corner of the slide.

The first problem, we are required to show that the number of Frenkel defects in a crystal of  $N$  atoms is given by... this is root of... Here  $E_f$  is the energy of formation of a Frenkel defect, and  $N'$  is the number of interstitial sites while  $N$  is the number of atoms in crystal.

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If  $E_v$  and  $E_i$  are the energies required to create a vacancy and an interstitial atom respectively, then the number of vacancies and interstitial atoms are given

$$n_v = N e^{-\frac{E_v}{k_B T}}$$

$$n_i = N' e^{-\frac{E_i}{k_B T}}$$

where  $N'$  is the number of interstitial sites. Since every vacancy creates an interstitial atom

$$n = n_v = n_i$$

We do this by writing the energy for the formation of a vacancy.

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$E_v$  - Energy of formation of a vacancy  
 $E_i$  - Energy of formation of an interstitial atom.

$n_v = N \exp\left(-\frac{E_v}{k_B T}\right)$        $n_v = n_i = n$   
 $n_i = N' \exp\left(-\frac{E_i}{k_B T}\right)$

$n = \sqrt{n_v \cdot n_i}$

And  $E_i$  is the energy of formation of an interstitial atom. Once these are given, the number of vacancy as we have already seen is just  $N \exp(-E_v / k_B T)$ ; and by the similar

argument, the number of interstitial is  $N$  prime exponential minus  $e$   $i$  by  $k_B T$ . And by definition the number of vacancies and the number of interstitial should be equal, so let us call it  $n$ .


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where  $n$  is the number of Frenkel defects

$$n^2 = n_v n_i = NN' e^{\frac{-(E_v + E_i)}{k_B T}}$$

Let  $E_f = E_v + E_i$


so that

$$n = \sqrt{NN'} e^{\frac{-E_f}{k_B T}}$$


So that  $n$  – the number of Frenkel defects is just  $n_v$  times  $n_i$  square root. So this will be  $N$ ,  $N$  prime square root is exponential minus  $e_v$  plus  $e_i$  by  $k_B T$ .

(Refer Slide Time: 04:03)

$$E_f = E_v + E_i$$


$$n = \sqrt{NN'} \exp\left(-\frac{E_f}{2k_B T}\right)$$


So we define the Frenkel energy for the formation of a Frenkel defects as sum of the energy required for forming a vacancy and the energy required for forming an interstitial atom. So defining like this, we get the result...

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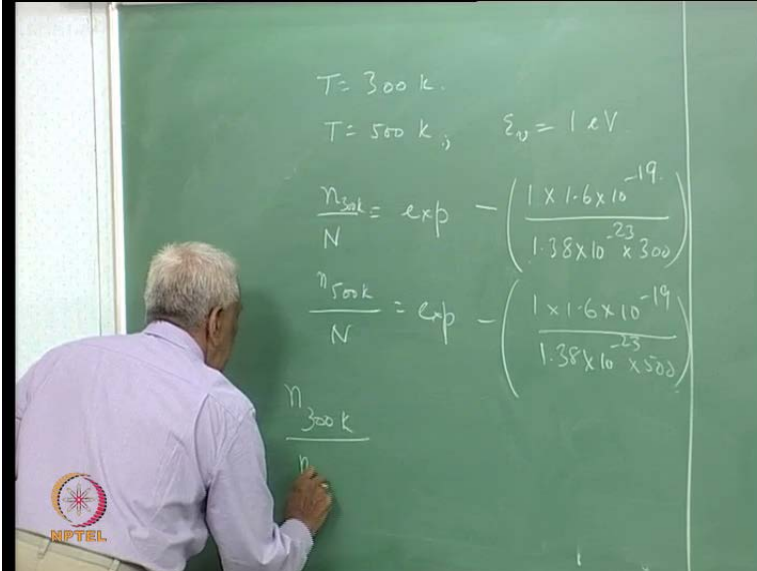
**Worked example 92**

**Problem**  
 Estimate the number of vacancies per atom in thermal equilibrium in a crystal at temperatures  $T = 300 \text{ K}$  and  $T = 600 \text{ K}$ , assuming that the energy required to form a vacancy is  $1 \text{ eV}$ .




Next, we required to estimate the number of vacancies per atom in thermal equilibrium at temperatures  $T$  equal to  $300 \text{ K}$ .

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$T = 300 \text{ K}$   
 $T = 500 \text{ K}; \quad \epsilon_v = 1 \text{ eV}$   
 $\frac{n_{300 \text{ K}}}{N} = \exp \left[ - \frac{1 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 300} \right]$   
 $\frac{n_{500 \text{ K}}}{N} = \exp \left[ - \frac{1 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 500} \right]$   
 $\frac{n_{300 \text{ K}}}{N}$



And T equal to 500 K if the activation energy, the energy for the formation of a vacancy is one electron volt.

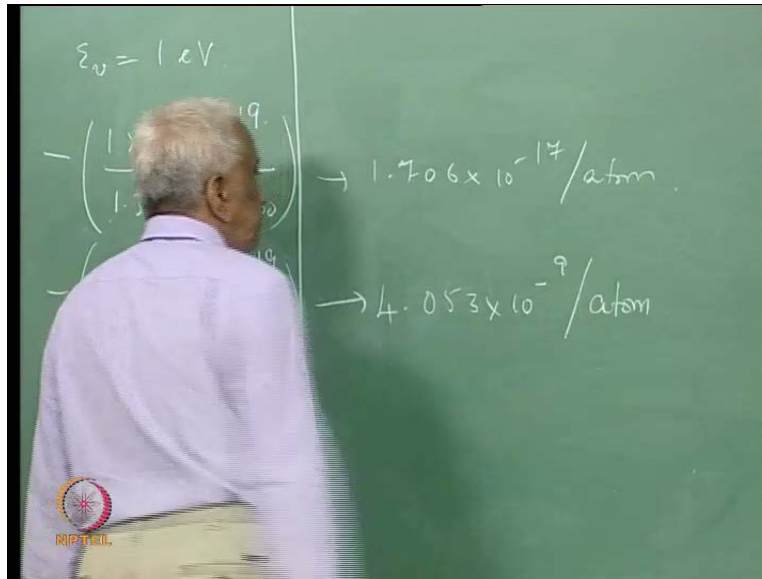
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**Solution**

$$\text{At 300K } k_B T = \frac{(1.38 \times 10^{-23} \times 300)}{1.6 \times 10^{-19}} = 0.0259 \text{ eV}$$
$$\frac{n}{N} = \exp\left(\frac{-E_v}{k_B T}\right) = \exp\left(\frac{-1}{0.0259}\right) = 1.706 \times 10^{-17} / \text{atom}$$
  
$$\text{At 600K } k_B T = \frac{(1.38 \times 10^{-23} \times 600)}{1.6 \times 10^{-19}} = 0.0518 \text{ eV}$$
$$\frac{n}{N} = \exp\left(\frac{-1}{0.0518}\right) = 4.053 \times 10^{-9} / \text{atom}$$


So it is a simple substitutional problem, so we have n by N – the number of vacancies by the number of atoms is just exponential minus 1 electron volt which is 1.6 into 10 to the power minus 19 by k B T which is 1.38 into 10 to the power minus 23 into 300 at 300 K. Similarly, n 500 K by N is exponential minus 1 electron volt, which is 1.6 into 10 to the power minus 19 by 1.38 into 10 to the power minus 23 into 500. So the ratio n 300 K by n 500 K, no we are ask to find these at 600 K, so this is also 600.

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So it is simply a question of finding this, so you get  $1.706 \times 10^{-17}$  per atom, and this works out to be  $4.053 \times 10^{-9}$  per atom. So by just heating it to 600 k from 300 k, you get an enhancement of the vacancy concentration by 8 orders of magnitude.

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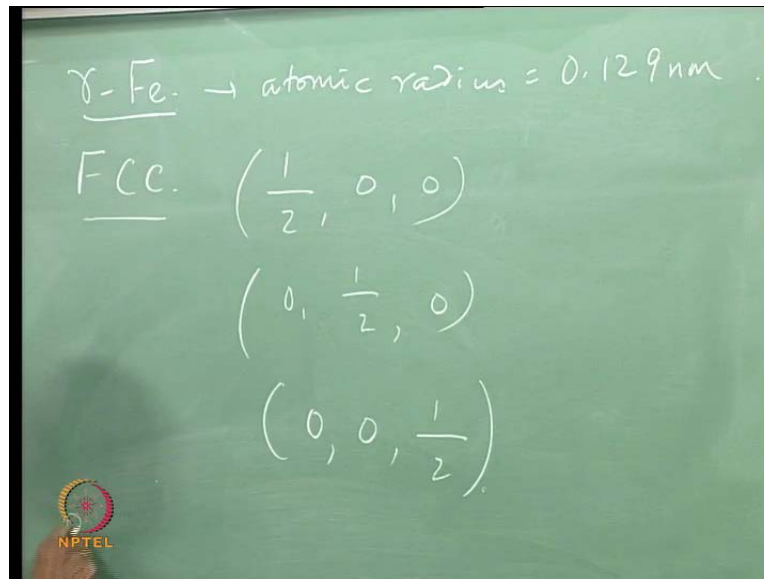
**Worked Example 93**

In an FCC lattice the largest interstitial voids occur at positions such as  $(1/2, 0, 0)$ ,  $(0, 1/2, 0)$ ,  $(0, 0, 1/2)$ , etc.  $\gamma$  Iron crystallizes in FCC structure and its atomic radius is 0.129 nm. Calculate the radius of the largest interstitial void in  $\gamma$  Iron.



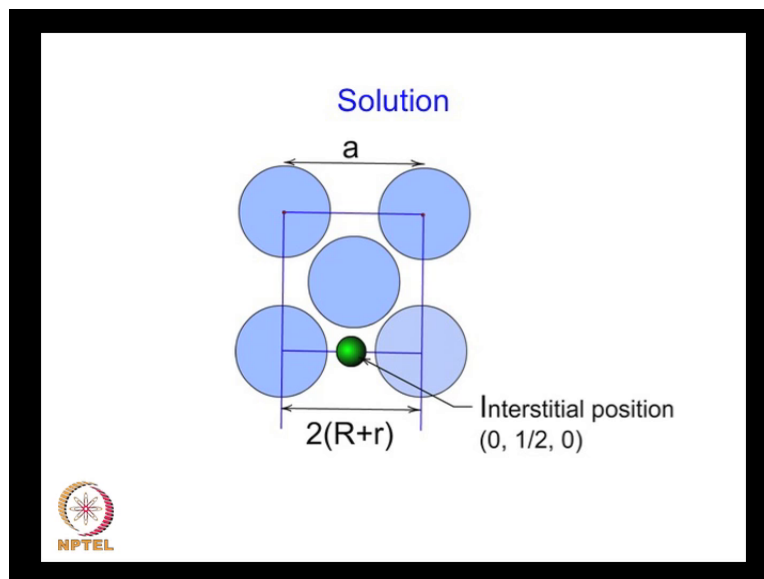
So, this is a very remarkable result. Next, we move on to consider, an FCC lattice in which the largest interstitial voids occur at positions.

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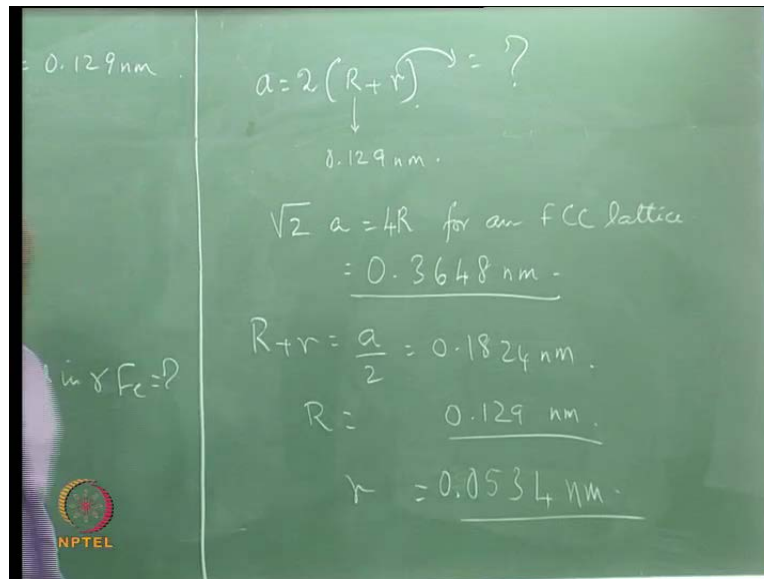
Such as half, 0, 0, these are the coordinates; 0, half, 0, and 0, 0, half centers and the edges. And this is the structure of gamma iron, which has an atomic radius of 0.129 nano meters. So we are ask to find the large radius, the largest interstitial voids the radius of... that is the question.

(Refer Slide Time: 09:02)



So to do this, again we are given the sides, so the figure shows how it is. You got the square phase and the interstitial position occurs at the center of the cube edge and if the radius of these the interstitial atoms is  $r$  - small  $r$  and the radius of the iron atom is capital  $R$  then.

(Refer Slide Time: 09:33)



The distance is the side of the cube is 2 into R plus r.


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In the figure one face of the FCC lattice is shown with an atom at interstitial site  $(0, 1/2, 0)$ . From the figure it can be seen that

$$a = 2(R + r)$$

where  $a$  is the lattice constant,  $R$  is the atomic radius of iron and  $r$  is the atomic radius of the interstitial atom.


For FCC,  $a$  and  $R$  are related by

$$\sqrt{2} a = 4R$$
$$a = \frac{4R}{\sqrt{2}} = 4 \times \frac{0.129}{\sqrt{2}} = 0.3648 \text{ nm}$$


So that is the lattice constant. And  $R$  is the atomic radius given as the 0.129 nano meters. And we are asked to find this. Now  $a$  and  $R$  are related by root 2  $a$  equal to for an FCC values – the face centered lattice, so that means so  $a$  will be 0.3648, so that is the lattice constant.



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$$R + r = \frac{a}{2} = \frac{0.3648}{2} = 0.1824 \text{ nm}$$
$$r = 0.1824 - R = 0.1824 - 0.129 = 0.0534 \text{ nm}$$


And  $R + r$  is simply  $a$  by 2, which is naught 0.1824, and  $R$  is 0.129. Therefore,  $r$  is difference between these two that is the radius of the largest interstitial.

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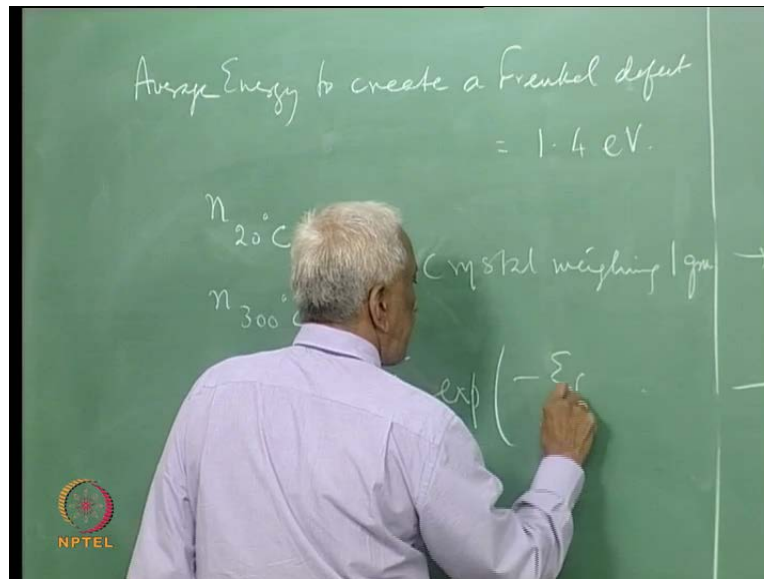
### Worked Example 94

**Problem**  
Average energy required to create a Frenkel defect in an ionic crystal is 1.4 eV. Calculate the ratio of Frenkel defects at 20°C and 300°C in 1 gram of the crystal.



Next we are told that the average energy required to create a Frenkel defect is given to be 1.4 electron volt in ionic crystal.

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So we are asked to calculate the ratio of Frenkel defects at 20 Celsius and 300 Celsius, in a crystal being one gram. So we know the expression for the number of Frenkel defects, we have already done this.

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**Solution**

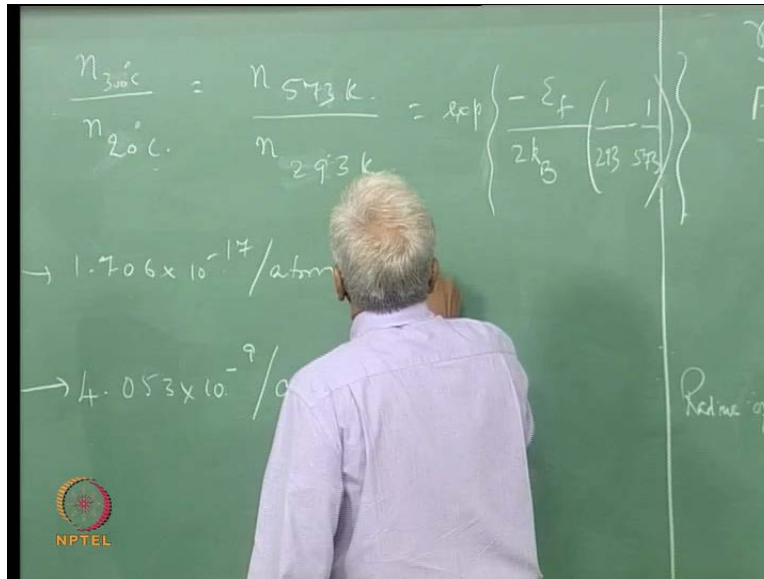
$$n = \sqrt{NN'} e^{\frac{-E_f}{k_b T}}$$

where  $n$  = number of Frenkel defects  
 $N$  = number of atoms  
 $N'$  = number of interstitial sites  
 $E_f$  = energy of formation of Frenkel defect



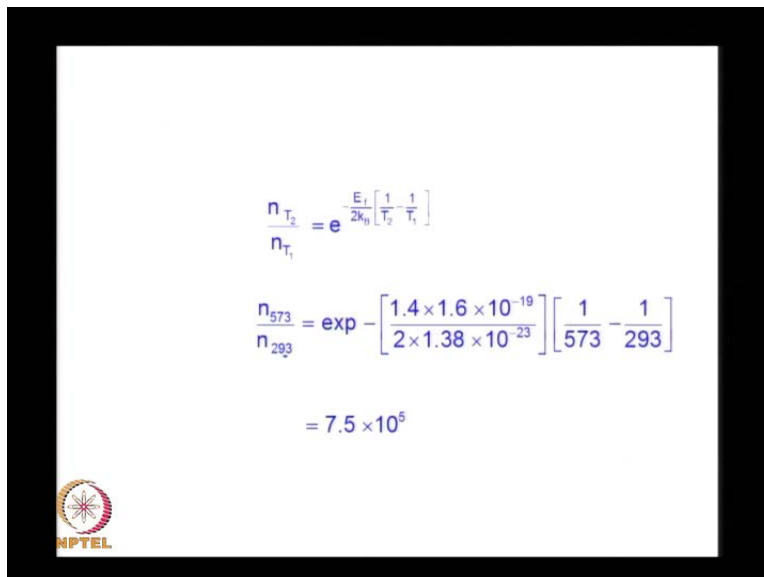
Where  $E_f$  is 1.4,  $N$  is the number of atoms, and we just take the ratio.

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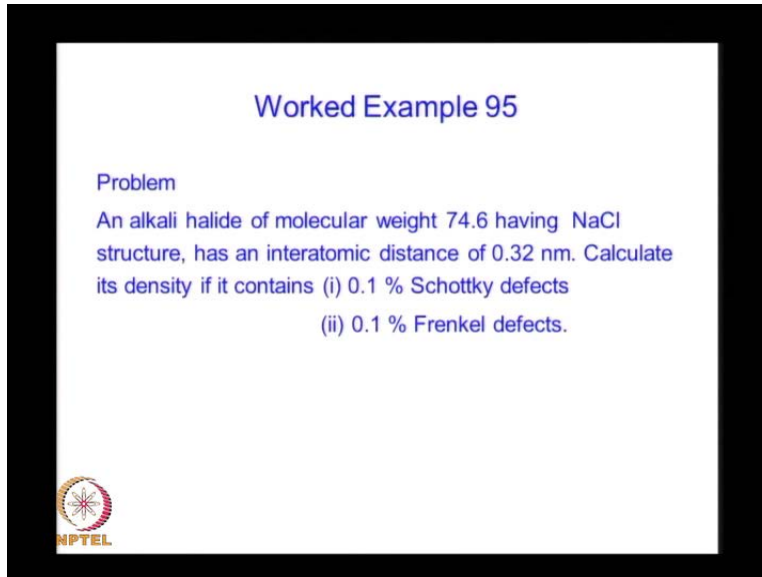
So n 20 Celsius by n 300 Celsius. So that is the same as 293 K and this is 573 K.

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So the ratio will be N and prime will cancel, so you will have exponential minus E f by 2 k B into 1 by 293 that is works out well it is the other way about it may write 300 k and 20 here. So this becomes 573 and this becomes 293, so that this will be this ratio works out to be 7.5 into 10 to the power 5. So the number of Frenkel defects by simply heating it from 20 Celsius to 300 Celsius increases by 5 orders of magnitude.


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**Worked Example 95**

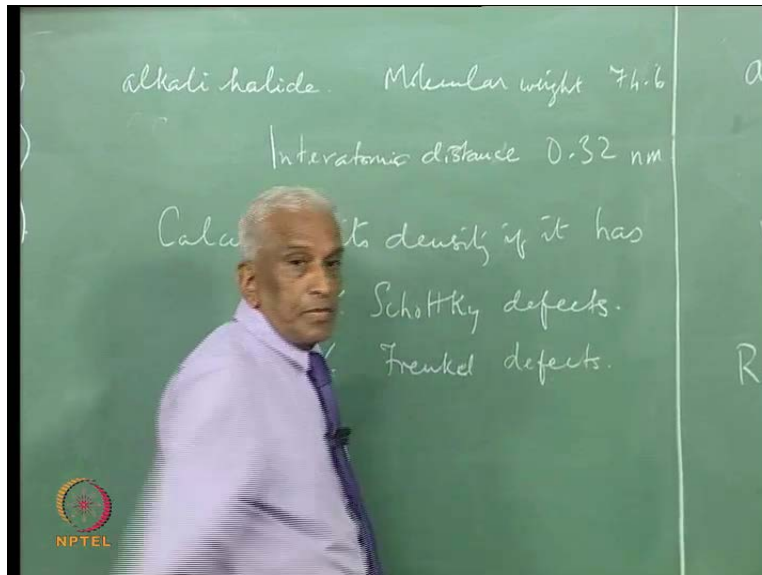
**Problem**

An alkali halide of molecular weight 74.6 having NaCl structure, has an interatomic distance of 0.32 nm. Calculate its density if it contains (i) 0.1 % Schottky defects  
(ii) 0.1 % Frenkel defects.



Next we are told that an alkali halide.


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alkali halide. Molecular weight 74.6

Interatomic distance 0.32 nm

Calculate its density if it has  
Schottky defects.  
Frenkel defects.



Such as a sodium chloride has a molecular weight of 74.6, inter atomic distance is given to be 0.32 nano meter. So we are ask to calculate density if it has 0.1 percent Schottky defect or 0.1 percent Frenkel defect. So the presence of defects of Schottky or Frenkel both will change the density of the crystal.

(Refer Slide Time: 15:52)

**Solution**


(i) The density of perfect crystal:  
Number of molecules/unit cell = 4

Weight of 4 molecules  $\frac{4}{6.023 \times 10^{26}} \times 74.6 = 4.95 \times 10^{-25}$  kg

Density =  $\frac{\text{wt. of 4 molecules}}{a^3}$

$a = 2 \times 0.32$  nm

Density =  $\frac{4.95 \times 10^{-25}}{(0.64 \times 10^{-9})^3} = 1.888 \times 10^{-3}$  kg/m<sup>3</sup>  
 $= 1.89 \times 10^3$  kg/m<sup>3</sup>




So we are asked to find this. Now in order to know this, we first calculate the density of the perfect crystal in the usual way.

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Density of perfect (defect-free) crystal.

4 molecules/unit cell.

Wt. of 4 molecules =  $\frac{4 \times 74.6}{6.023 \times 10^{26}}$   
 $= 4.95 \times 10^{-25}$  kg



Perfect means defect free for which we are given the molecular weight and this is the sodium chloride structure, so the number of molecules per unit cell is 4. So the weight of 4 molecules which occupy the unit cell is 4 times 74.6 divided by... That works out to be 4.95 into 10 to the power minus 25 kilograms.

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Density of perfect crystal =  $\frac{4.95 \times 10^{-25} \text{ kg}}{(0.32 \times 10^{-9})^3 \text{ m}^3}$   
 $= 1.89 \times 10^3 \frac{\text{kg}}{\text{m}^3}$

0.1% Schottky defects: 1 in 1000 molecules

Volume change =  $\frac{1001}{1000}$

NPTEL

So this is the density and volume of the unit cell is just a cube, where  $a$  is given to be, so the density of the perfect crystal is just ratio of these two and that will be 1.89.

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(ii) Schottky defect:  
1 defect in 1000 molecules  
Volume increases by the ratio  $\frac{1000}{1001}$   
molecular weight decreases by the ratio  $\frac{999}{1000}$

Density =  $1.888 \times 10^3 \times \frac{1000}{1001} = 1.886 \times 10^3 \text{ kg/m}^3$

(ii) Frenkel defect: There is no change in density

NPTEL


Now if we have Schottky defect 1 percent then what happens, you have 0.1 percent. Yes, so this is 1 in 1000 molecules, so the number of Schottky defect is just the number of molecules divided by 1000.

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(ii) Schottky defect:  
1 defect in 1000 molecules  
Volume increases by the ratio  $\frac{1001}{1000}$

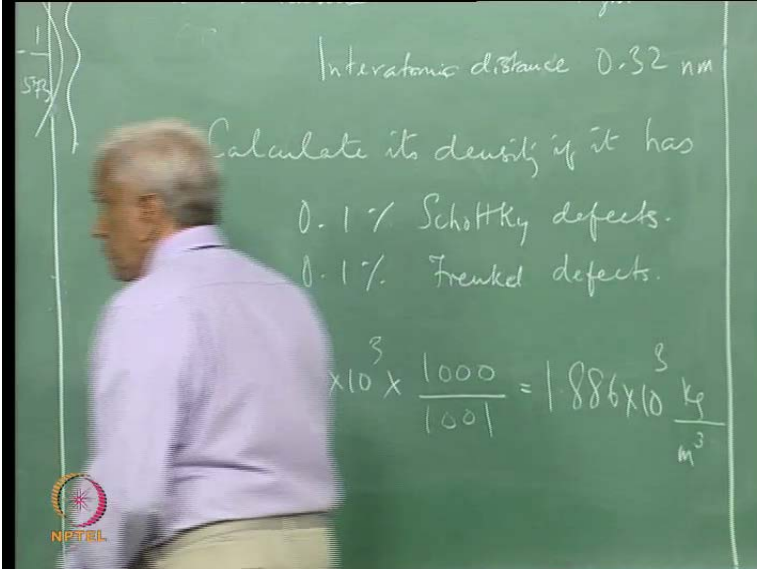
$$\text{Density} = 1.888 \times 10^3 \times \frac{1000}{1001} = 1.886 \times 10^3 \text{ kg/m}^3$$

(ii) Frenkel defect: There is no change in density




And therefore, the volume change, we are interested in the density change, so volume. So if I have 1000 molecules, now the volume due to the Schottky defect increases by the factor 1001 by 1000, because there is one Schottky defect. Whereas, in the case of Frenkel defect, since it is a vacancy plus an interstitial, therefore, whatever be the concentration, there is no change in density. And in this case, since the volume changes by this, decreases by a factor.

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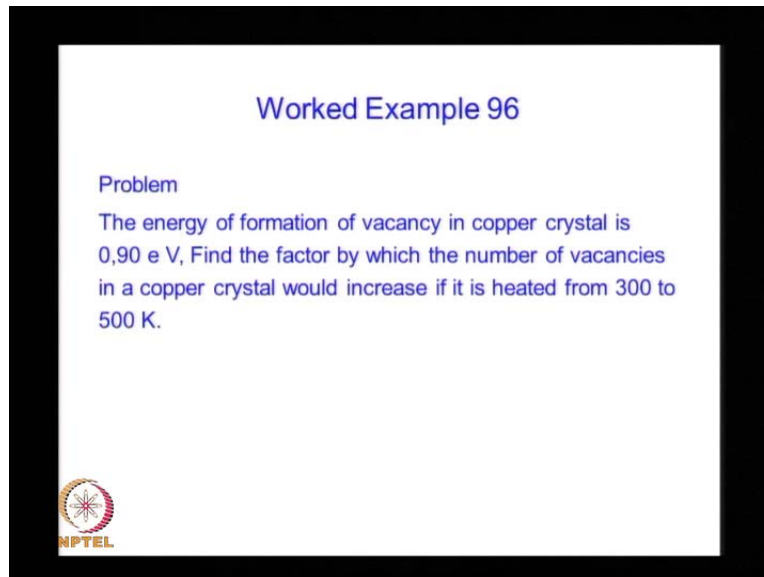


Interatomic distance 0.32 nm  
Calculate its density if it has  
0.1% Schottky defects.  
0.1% Frenkel defects.

$$1.888 \times 10^3 \times \frac{1000}{1001} = 1.886 \times 10^3 \frac{\text{kg}}{\text{m}^3}$$



Therefore the density is, go the density there 1.89 into 10 to the power 3 into this factor 1000 by 1001, and that would be 1.886...

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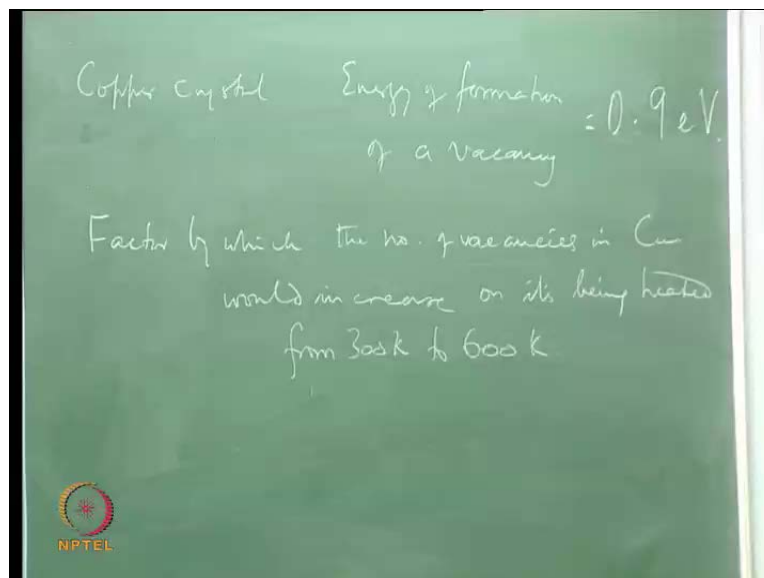
**Worked Example 96**

**Problem**  
The energy of formation of vacancy in copper crystal is 0.90 eV. Find the factor by which the number of vacancies in a copper crystal would increase if it is heated from 300 to 500 K.




Next we are told the crystal of copper.

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Copper crystal      Energy of formation  
   of a vacancy = 0.9 eV.

Factor by which the no. of vacancies in Cu  
would increase on its being heated  
from 300 K to 600 K.




In which the energy of formation of a vacancy is given to be 0.9 electron volts. Find the factor by which the number of vacancies in copper would increase if it is heated from 300 300 K to 600 K, again relatively a straightforward, question to answer.



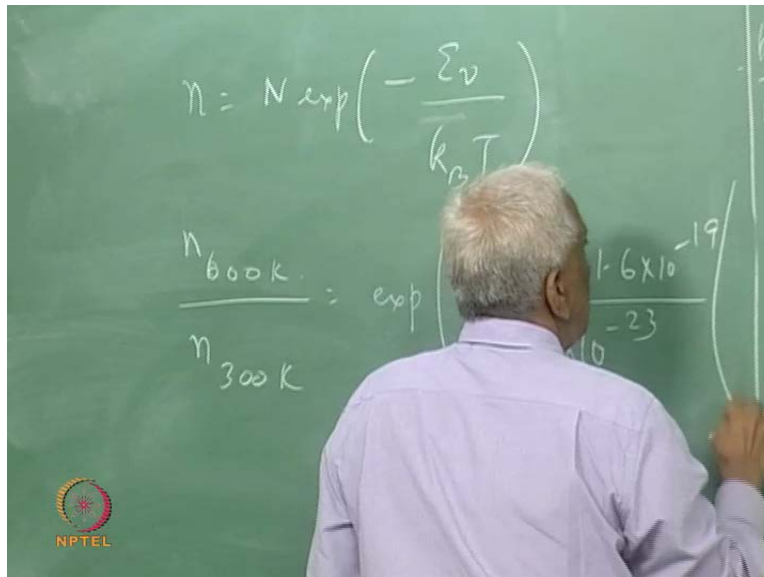
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$$n = N \exp\left\{\frac{-E_v}{k_B T}\right\}$$
$$n_{300k} = N \exp\left\{\frac{-E_v}{k_B 300}\right\}$$
$$n_{500k} = N \exp\left\{\frac{-E_v}{k_B 500}\right\}$$
$$\frac{n_{500k}}{n_{300k}} = \exp\left\{\frac{-E_v}{k_B}\left(\frac{1}{500} - \frac{1}{300}\right)\right\}$$
$$= 10^6$$

 (after substitution of the values for  $\frac{E_v}{k_B}$ )

Use this standard expression, the number of vacancies.

(Refer Slide Time: 22:45)



$$n = N \exp\left(\frac{-E_v}{k_B T}\right)$$
$$\frac{n_{600K}}{n_{300K}} = \exp\left(\frac{-1.6 \times 10^{-19}}{1.38 \times 10^{-23}}\right)$$

So we have  $n_{600K}$  by  $n_{300K}$ . That will be the ratio will simply the exponential minus  $0.91.6$  into  $10$  to the power minus  $19$  by  $1.38$  into  $10$  to the power minus  $23$  into  $1$  by... So if you calculate this that works out to be  $10$  to the power  $6$ .

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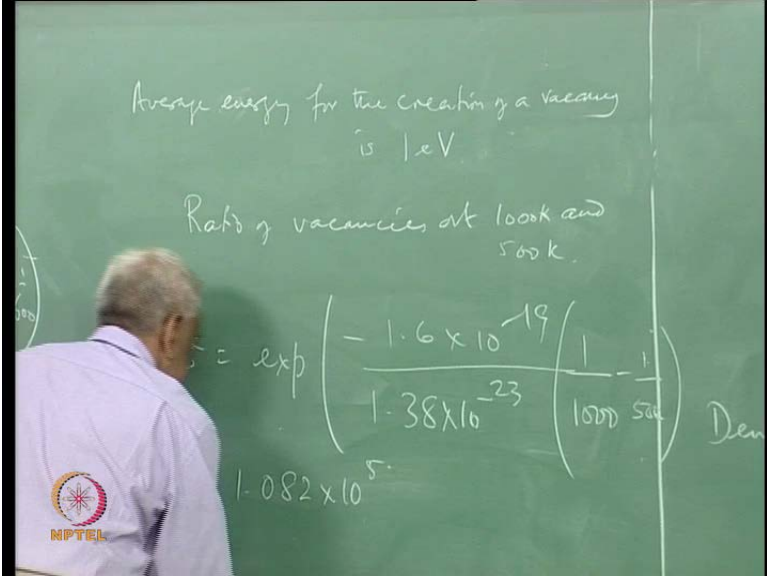
**Worked Example 97**

**Problem**  
Average energy required to create a vacancy in a metal is 1 eV .Calculate the ratio of vacancies at 1000 K to that at 500 K.



We are told that in a metal the average energy.

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Average energy for the creation of a vacancy is 1 eV

Ratio of vacancies at 1000k and 500k

$$n = \exp\left(\frac{-1.6 \times 10^{-19}}{1.38 \times 10^{-23} \left(\frac{1}{1000} - \frac{1}{500}\right)}\right)$$

Den

$1.082 \times 10^5$




Needed for the creation of a vacancy in a metal is one electron volt. So calculate the ratio of vacancies at 1000 k and 500 K. Again a very simple question, n 1000 K by n 500 K is exponential minus... That is again comes to 1.082 into 10 to the power 5. These are all just to give you an order of magnitude idea about the relative concentration of vacancies and other defects when one heats the metal as we go to higher temperature.

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**Worked Example 98**

**Problem**  
A gold wire is heated to different temperatures, rapidly quenched into water at each temperature and the resistance measured at 4 K. The following results are obtained.

$T^{\circ}\text{C}$	$\Delta R \times 10^{-2}$ $\mu\Omega \text{ cm}$
597	0.13
647	0.22
697	0.48
747	0.78
797	1.20
842	2
897	3



Next we have data concerning a resistance.


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change in  
Resistance of a Au-wire after rapid quenching  
(4K) in water following heating.

↓

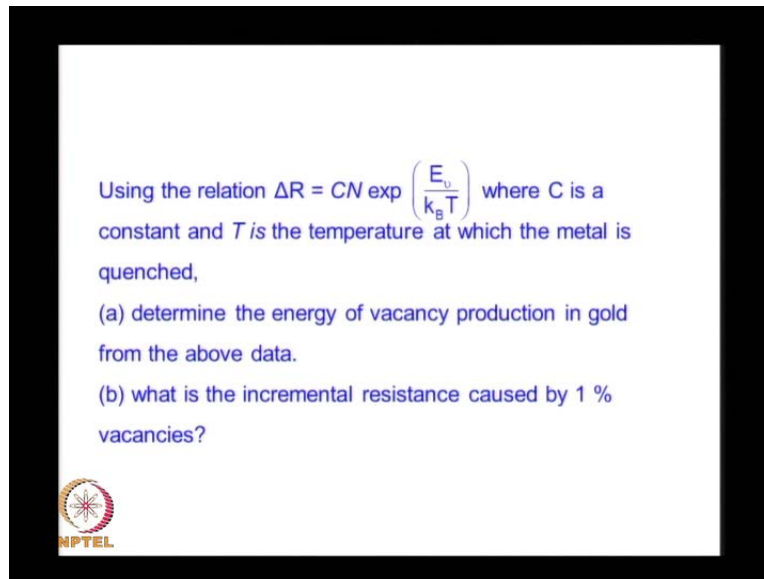
$$\Delta R = C N \exp\left(\frac{\Sigma_v}{R_B T}\right)$$

Determine  $E_0$



The change in resistance of a gold wire is given at different temperature, the gold wire is heated to different temperature and then rapidly quenched into water at each temperature and the resistance is measured at four K, after rapid quenching in water following heating. So the temperatures to which, there heated are all given in tabular form.


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Using the relation  $\Delta R = CN \exp\left(\frac{E_v}{k_B T}\right)$  where  $C$  is a constant and  $T$  is the temperature at which the metal is quenched,

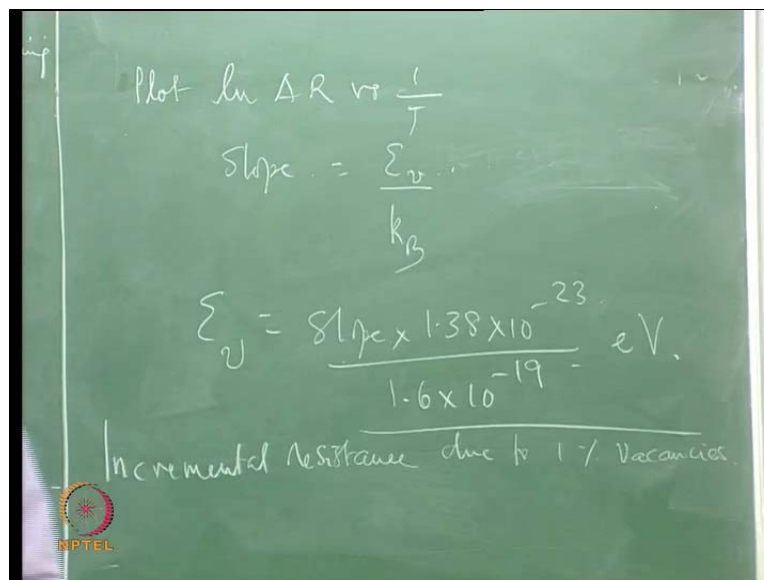
(a) determine the energy of vacancy production in gold from the above data.

(b) what is the incremental resistance caused by 1 % vacancies?



And we are given the relation  $\Delta R$ , the change in resistance is some constant  $C$  times  $N$  exponential minus  $E_v$ .  $C$  is a constant and  $T$  is the temperature at which, to which it is heated. So we are asked to determine the energy of vacancy production, determine  $E_v$ . In order to do that from this relation we can that  $\log \Delta R$  is  $\log C$  plus  $\log N$  plus  $E_v$  by  $k_B T$ .

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Plot  $\ln \Delta R$  vs  $\frac{1}{T}$

Slope =  $\frac{E_v}{k_B}$

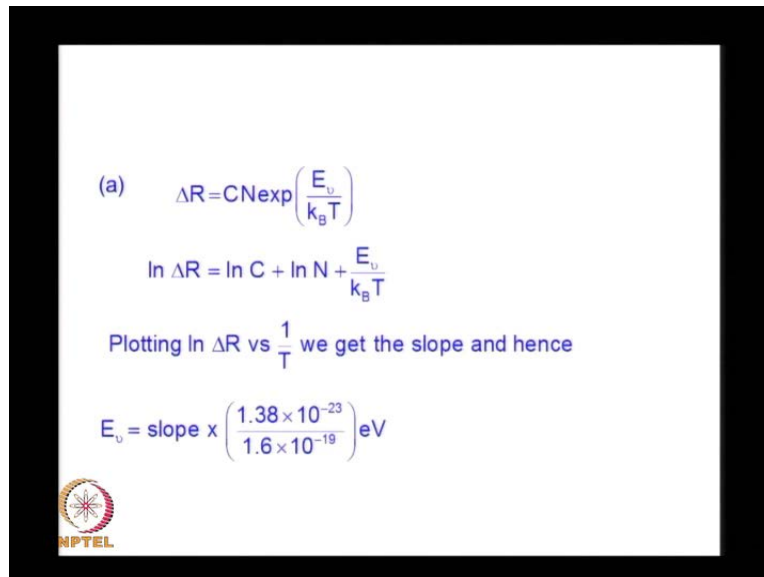
$E_v = \frac{\text{Slope} \times 1.38 \times 10^{-23}}{1.6 \times 10^{-19}} \text{ eV.}$

Incremental Resistance due to 1% Vacancies




So if one plots  $\log \Delta R$  from the given data as the function of versus one by  $T$ . The slope gives the energy of the vacancy.

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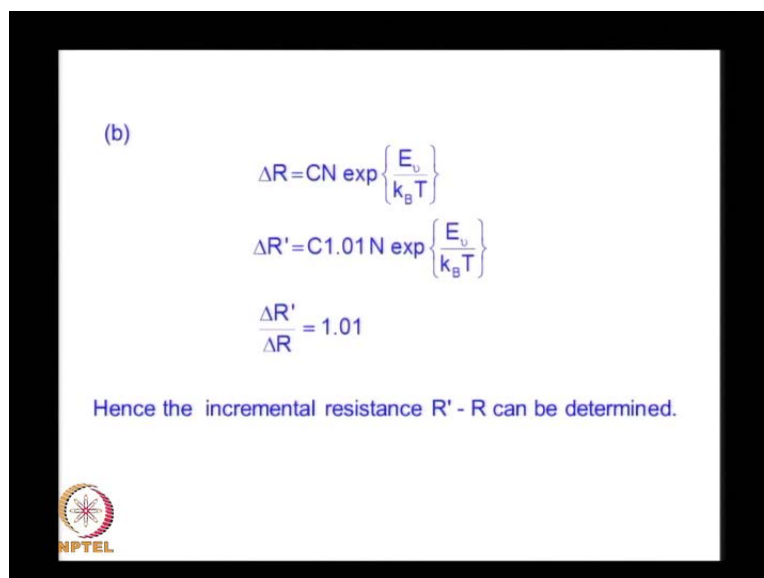


(a) 
$$\Delta R = CN \exp\left(\frac{E_v}{k_B T}\right)$$
$$\ln \Delta R = \ln C + \ln N + \frac{E_v}{k_B T}$$
Plotting  $\ln \Delta R$  vs  $\frac{1}{T}$  we get the slope and hence
$$E_v = \text{slope} \times \left(\frac{1.38 \times 10^{-23}}{1.6 \times 10^{-19}}\right) \text{eV}$$




So this is the slope, so  $E_v$  will be slope times the Boltzmann constant and if you want to find it in electron volt divide by  $10$  to the power minus  $19$ , that would give it in... Since this involves plotting this is simply given as an expression, one can do this and see. And we are also asked to calculate the incremental resistance caused by 1 percent vacancies.

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(b) 
$$\Delta R = CN \exp\left\{\frac{E_v}{k_B T}\right\}$$
$$\Delta R' = C1.01N \exp\left\{\frac{E_v}{k_B T}\right\}$$
$$\frac{\Delta R'}{\Delta R} = 1.01$$
Hence the incremental resistance  $R' - R$  can be determined.



Again one uses the data, and find  $\Delta R$  from this data, so it will be 1 percent increase in vacancy.

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$$\Delta R' = 1.01 N \cdot \exp\left(\frac{\epsilon_v}{k_B T}\right)$$
$$\frac{\Delta R'}{\Delta R} = 1.01$$
$$\Delta R' - \Delta R$$


So 1.01 N exponential, so that is out modified. So this is delta R prime, so delta R prime by delta R just 1 point naught one. So one can find the delta R prime minus delta R, that is the incremental resistance.

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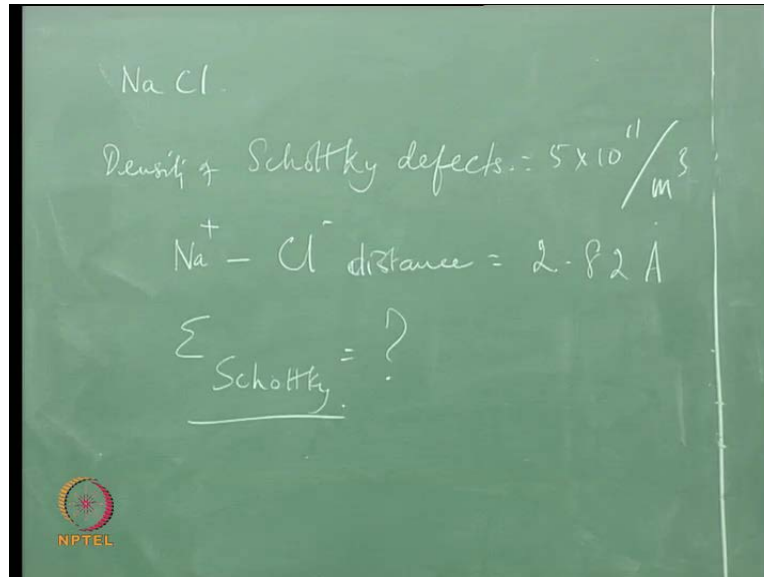
**Worked Example 99**

**Problem**  
Density of Schottky defects in a sample of NaCl is  $5 \times 10^{11}/\text{m}^3$  at 25°C.  $\text{Na}^+ - \text{Cl}^-$  distance is 2.82 Å. Calculate the average energy required to create a Schottky defect



The last problem concern, the density of Schottky defects.

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Which is given in a sample of sodium chloride, density means concentration that is given as 5 into 10 to the power 11 per meter cube. And the distance of the sodium plus to the chlorine minus ion distance, the sodium chloride is also given to be 2.82 angstrom unit. So we are asked to calculate the average energy for the creation of Schottky defect that is the question.

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Number of ion pairs per unit volume =  $\frac{1}{(2.82 \times 10^{-10})^3}$

No of Schottky defects per unit volume  
No of ion pairs per unit volume =  $\frac{5 \times 10^{11}}{4 \times 10^{28}}$

=  $1.25 \times 10^{-17}$

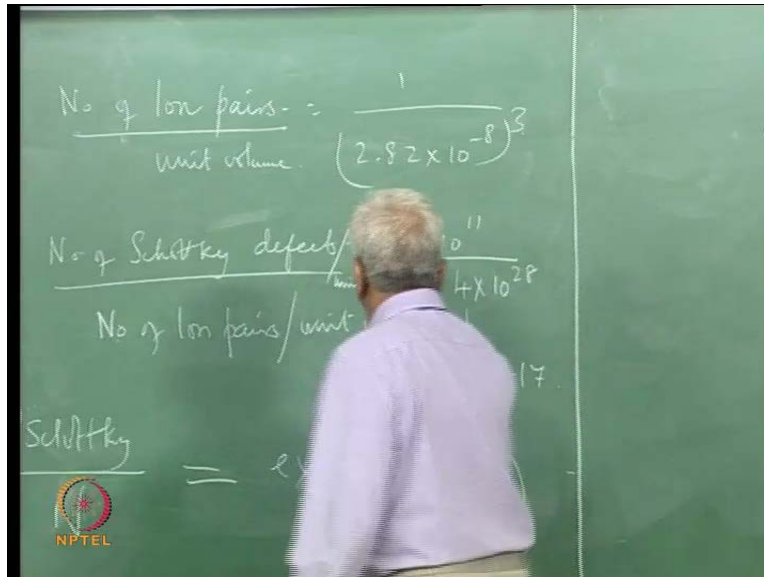
=  $\exp \frac{(-E_{\text{Schottky}})}{2k_B T}$

Taking T as 300 K we get

$E_{\text{Schottky}}$  as 1.971 eV

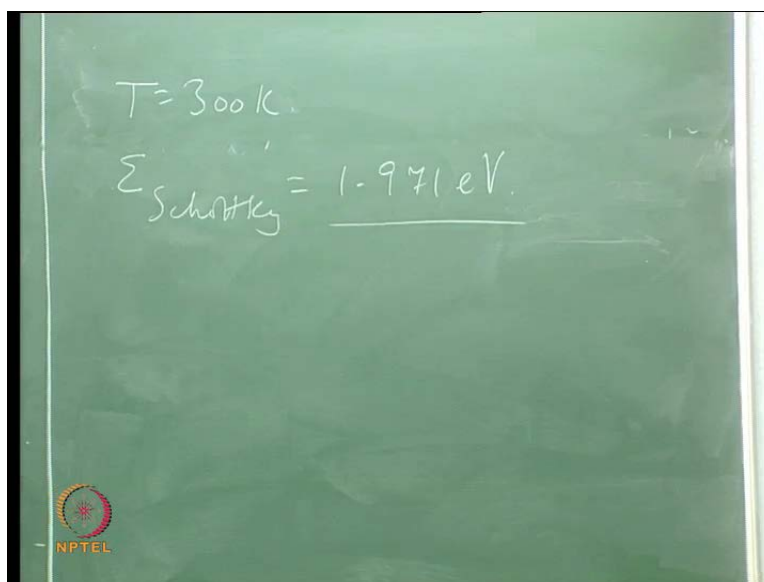
So in order to do this, since see Schottky defect involves vacancies in both the anion and cation sites simultaneously, so we must find the number of ion pairs in the given data.

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So that will be 1 by 2.82 into 10 to the power minus 8 cube, that is the lattice volume per unit volume. And number of Schottky defects, in order to calculate this, we have 5 into 10 to the power 11 is given. So that divided by the number of ion pairs both per unit volume. We take the ratio of these 2 this works out to be 4 into 10 to the power 28, so that will give me 1.25 into 10 to power minus 17. And that is the ratio of N by and that is given to be exponential minus E Schottky by 2 k B T. So since this is known to be equal to this.

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Therefore, we can the temperature as 300 K and get the energy of Schottky pair as 1.971 electron volts.