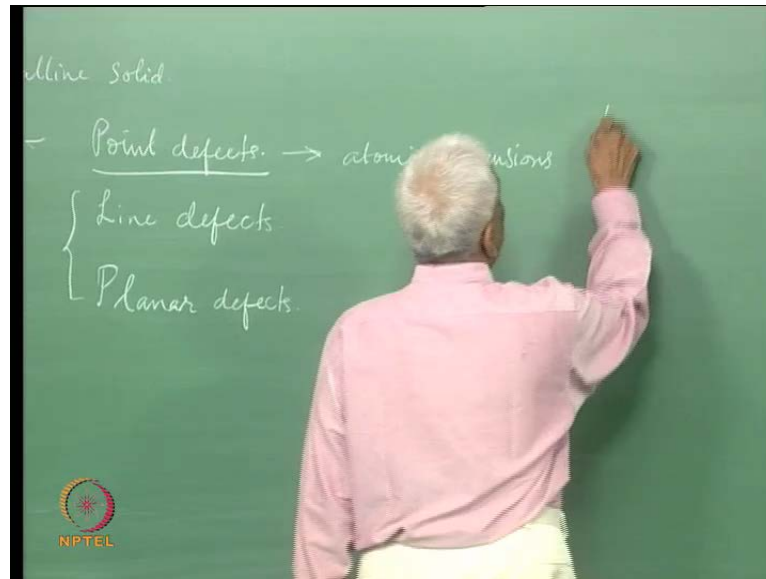


**Condensed Matter Physics**  
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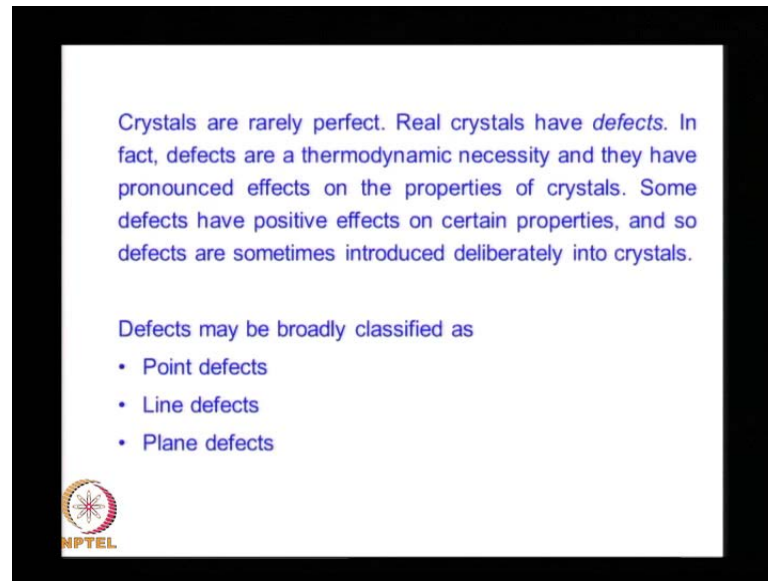
**Lecture - 38**  
**Defect in Solids-Point Effect**

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So far we have been considering the solid as a perfect one perfect crystalline solid in other words, there is a regular periodic arrangement or the atoms or molecules in the entire throughout the entire lattice structure of the crystal. So, we all know that this is a and approximation this is idealization or the actual situation in actual practice defect of different kinds occur. And as usual see defects in solids of various kinds or thermodynamic necessity it is not just that they occur, but they actually are essential for maintaining thermodynamic equilibrium of the solid, therefore the presence of defects is a fact which must be considered taken into account in order to discuss the properties of real crystal line solids. So, we will spend a little time in this lecture, and in the next to consider the presence of defects of various kinds in solids, and to some extent there in flames on the physical properties.


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Crystals are rarely perfect. Real crystals have *defects*. In fact, defects are a thermodynamic necessity and they have pronounced effects on the properties of crystals. Some defects have positive effects on certain properties, and so defects are sometimes introduced deliberately into crystals.

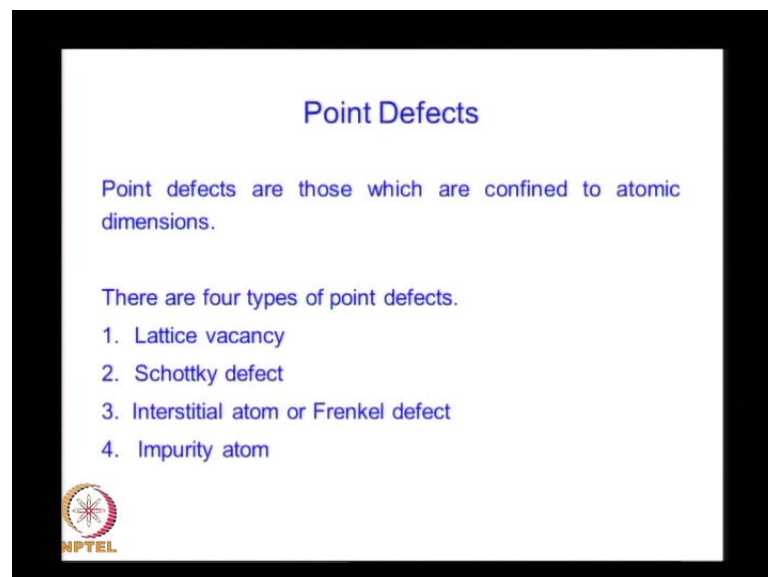
Defects may be broadly classified as

- Point defects
- Line defects
- Plane defects



Now these defects are of different kinds there can be what are known as point defects. We considered the point defects today, but there are other defects also such as line defects this we already saw this in lecture band in the name of topological defects and called them dislocations, and there can be also plainer defects in three-dimensional solids.

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### Point Defects

Point defects are those which are confined to atomic dimensions.

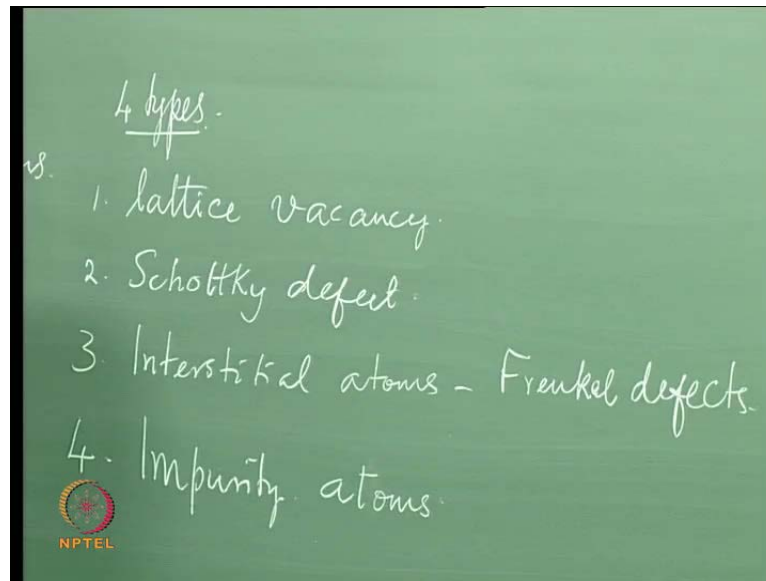
There are four types of point defects.

1. Lattice vacancy
2. Schottky defect
3. Interstitial atom or Frenkel defect
4. Impurity atom



.So, these will consider the next lecture, today we will focus on point defects. So, point defects by the very name or defects, which are of atomic dimensions.

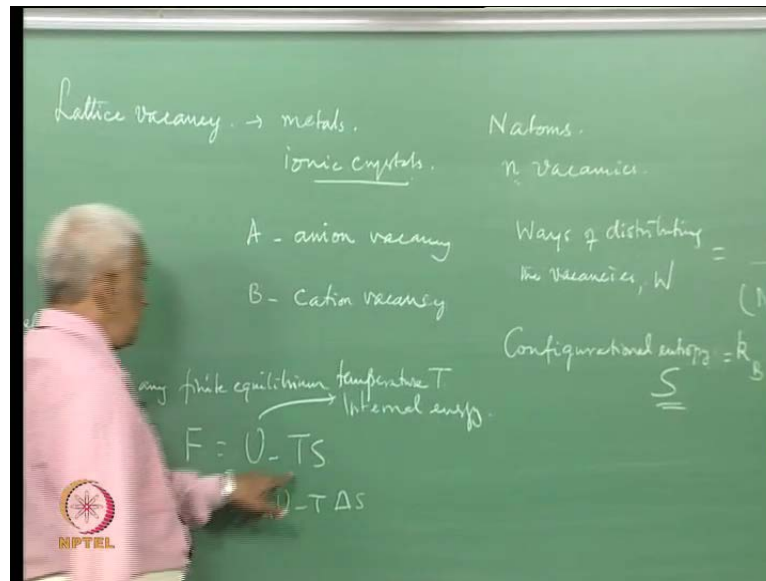
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We can think of basically four types of point defects as follows a lattice vacancy which means that an atom or molecule, which is supposed to be in a lattice site is missing and vacancies created in its place. Then there is what is known as Schottky defect we will discuss in these things in detail we will just enumerate it. Now then the third one is known as interstitial atoms, which means atoms which are displaced from the regular lattice sites under squeeze under interspace between the atoms in the interstices. So, they are called they are also known as Frenkel defects then the fourth type is an actually an impurity as we saw in the case of semiconductor, which are deliberately doped with silicon or Germanium which are deliberately doped with impurities or even drive valence and impurities which are different atoms.

So, these atoms got and occupy the position either an interstitial position or a vacant site in the regular lattice. So, they are impurities which occur in. So, they all... So, profoundly modified as we have seen in the case of extrinsic semiconductor they properties of the semiconductor. So, this can also happen in metals and other solids.

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So, these are the four main types of point defects, we will consider one by one first the lattice vacancy this can occur because of imperfect packing during crystallization of the solid or, because the atoms have been dislodged from their equilibrium positions because of thermal vibrations at high temperatures. This can occur in metals and ionic crystals at high temperatures.

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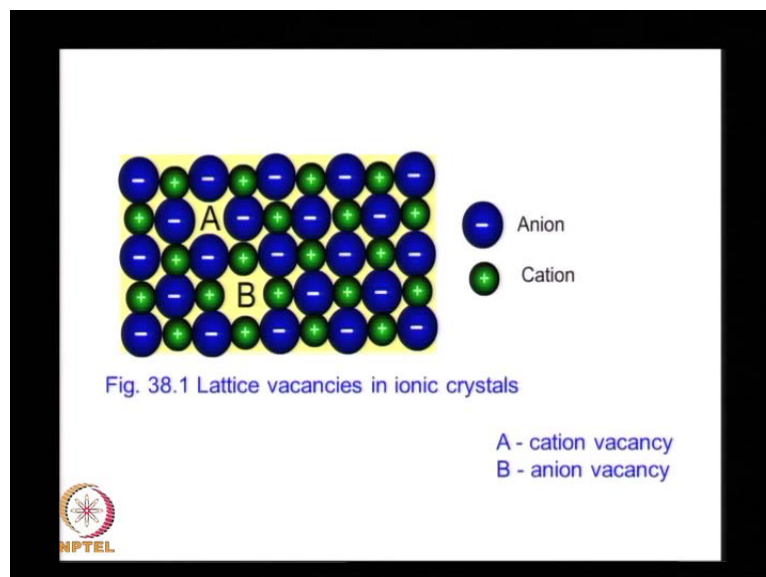



Figure 38.1 shows the presence of such vacancies in an ionic crystal. The vacancies can be in the site of an anion or it can be in a cation site, and an ionic crystal has anions as well

as cation the vacancies can be in the place of an ion or in the place of anion. So, both can create vacancies.

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• In a crystal of  $N$  atoms, if we remove  $n$  atoms from their proper sites, (forming  $n$  vacancies) these may be distributed in  $\frac{N!}{n!(N-n)!}$  ways among the  $n$  possible sites. This leads to a configurational entropy

$$\Delta S = k_B \ln \frac{N!}{n!(N-n)!} \quad (38.1)$$


Now, we mention that the present vacancies is thermodynamic necessity in order to understand this let us follow the following argument suppose the question has  $N$  atoms we just investigate the situation where in addition to these  $N$  atoms there are also small number  $N$  number vacancies . So, of the  $N$  atoms this many atoms small  $n$  are removed in order to create a vacancies. So, there are is  $N$  vacancies in a total of  $N$  atoms. So, there are many waves of choosing or distributing these vacancies. So, this waves of distributing the vacancies this will be given by usual formula. So, these are the total number of ways, and because of this there is a configurationally disorder and therefore, and entropy associated with it which is given by the famous Boltzmann formula  $k_B \ln$  suppose recall  $w$ . So, this is  $s$ . So, there is a constant at any finite temperature  $T$  equilibrium temperature  $T$ , we know that the thermodynamic equilibrium as established by minimizing the free energy associated with it.

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where  $k_B$  is the Boltzmann constant. The free energy of the system is

$$\Delta F = \Delta U - T\Delta S \quad (38.2)$$

$\Delta U$  is the internal energy given by

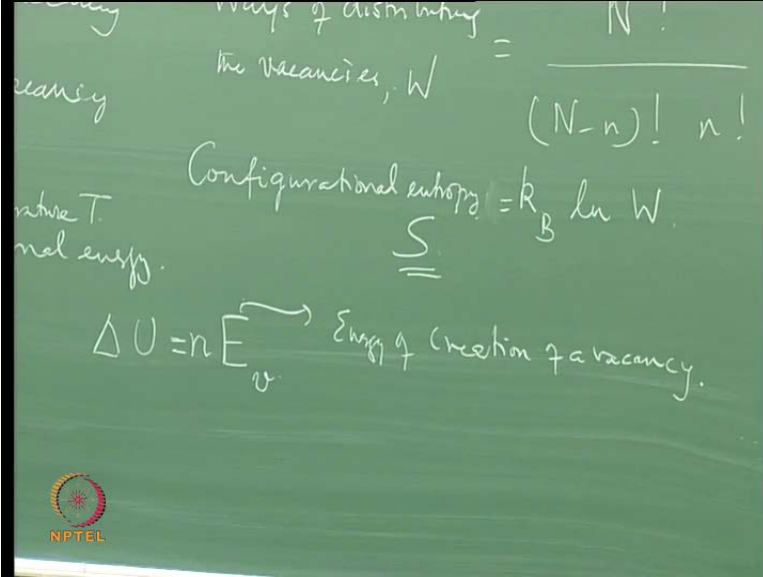
$$\Delta U = nE_v \quad (38.3)$$

where  $E_v$  is the energy of formation of a vacancy (i.e. the energy required to transfer an atom from the lattice site within the crystal lattice to surface of the crystal). Using (38.1) and (38.3) in (38.2)

$$\Delta F = nE_v - k_B T \ln \frac{N!}{n!(N-n)!} \quad (38.4)$$


So, this free energy will be  $F$  equals  $U$  minus  $T S$  we neglect a small associated with a possible volume change. So, if that is. So, the  $\Delta F$  is  $\Delta U$  minus  $T \Delta S$  at constant temperature, where  $U$  is be internal energy  $S$  is given here and  $T$  is the temperature

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ways of distribution =  $\frac{N!}{(N-n)! n!}$

the vacancies,  $W = \frac{N!}{(N-n)! n!}$

Configurational entropy =  $k_B \ln W$

$\Delta U = n E_v \rightarrow$  Energy of creation of a vacancy.



Now,  $\Delta U$  is due to creation these vacancies suppose  $E$  is the energy associated with the creation of a single vacancy, and there are  $N$  such vacancies. So, this would be the

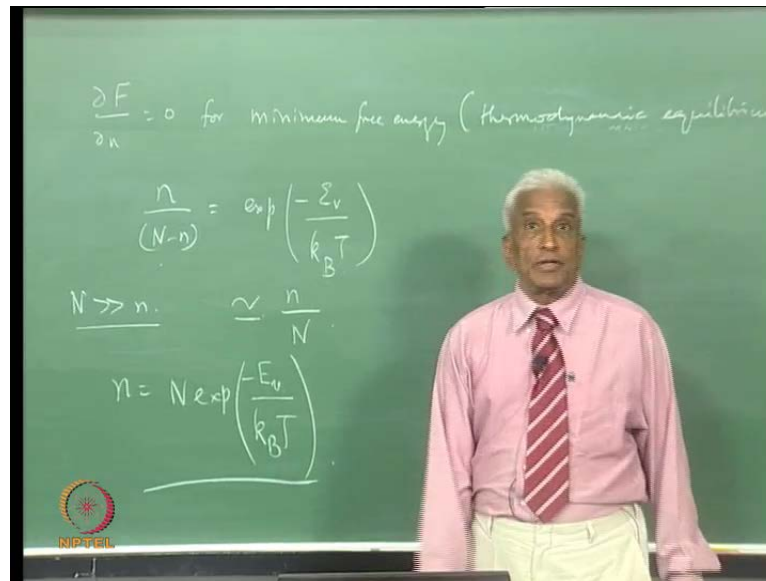
change internal energy due to the creation of N vacancies. this is the energy of creation of a vacancy.

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The image shows a green chalkboard with handwritten mathematical derivations. At the top, the equation is written as  $\Delta F = nE_v - T k_B \ln \left\{ \frac{N!}{(N-n)! n!} \right\}$ . Below this, it is noted that  $N$  is very large, and Stirling's formula is applied. The derivation shows the expansion of  $\ln N!$  as  $N \ln N - N$  and  $\ln(N-n)!$  as  $(N-n) \ln(N-n) - (N-n)$ . The final simplified expression for  $\Delta F$  is  $nE_v - k_B T \left\{ N \ln N - (N-n) \ln(N-n) - n \ln n \right\}$ . An NPTEL logo is visible in the bottom left corner of the chalkboard image.

So, we have to minimize delta F in other words in order to do this let us write delta F explicitly in order to evaluate these where factorial are large number of atoms N very large then we can use sterling formula which is a very good approximation in such situations. So, there which says  $\log N$  factorial is  $N \log N$  minus  $N$  and same for any other the like an  $N$  minus  $N$ . So, using this we can write this as using sterling formula. So, this cancel  $S$  of leaving as with. So, let us see changing free energy and we want this to be a minimum for a minimum the derivative with respect to  $N$  small  $n$  of the free energy should be set equal to 0.

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So, for minimum free energy for thermodynamic equilibrium. So, differentiating this we find by simplifying.

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Minimizing the free energy (i.e.  $\frac{d(\Delta F)}{dn} = 0$ ) we get


$$\frac{n}{N-n} = \exp\left(\frac{-E_v}{k_B T}\right) \quad (38.5)$$

Equation (38.5) can be obtained by using Stirling's formula  
 $\ln x! = x \ln x - x$

Since  $N \gg n$ , Eq. (38.5) can be written as

$$n \approx N \exp\left(\frac{-E_v}{k_B T}\right) \quad (38.6)$$

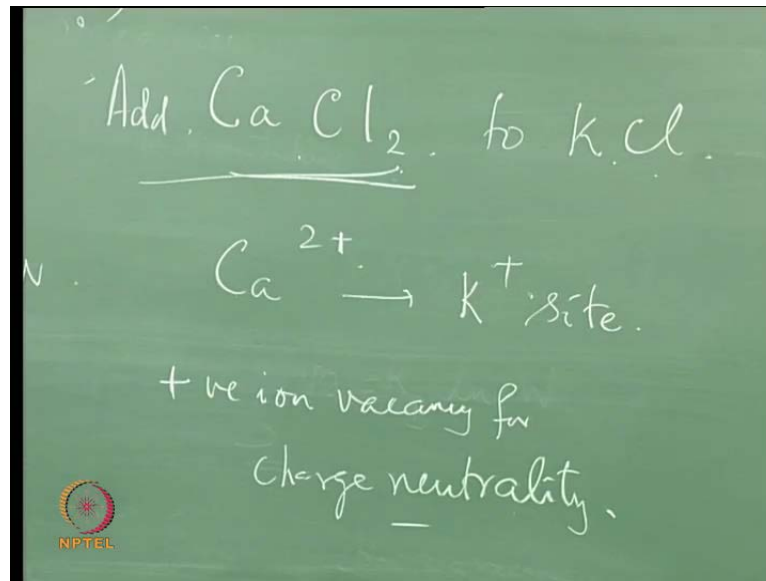
$E_v$  is normally of the order of 1 eV. For  $E_v = 1\text{eV}$ , at a temperature  $T = 1000\text{ K}$ ,  $n/N = 10^{-5}$ , i.e. the proportion of vacancies is 0.001 %.



Since  $N$  is very large compared to  $n$  we can just say this is equal to  $N$  by  $n$ . So, that we can get an expression  $n = N \exp(-E_v / k_B T)$  that tells you the number of vacancy in as a function of total number of atoms, and the energy creating the vacancy and absolute temperature  $k_B$  is the Boltzmann constant.



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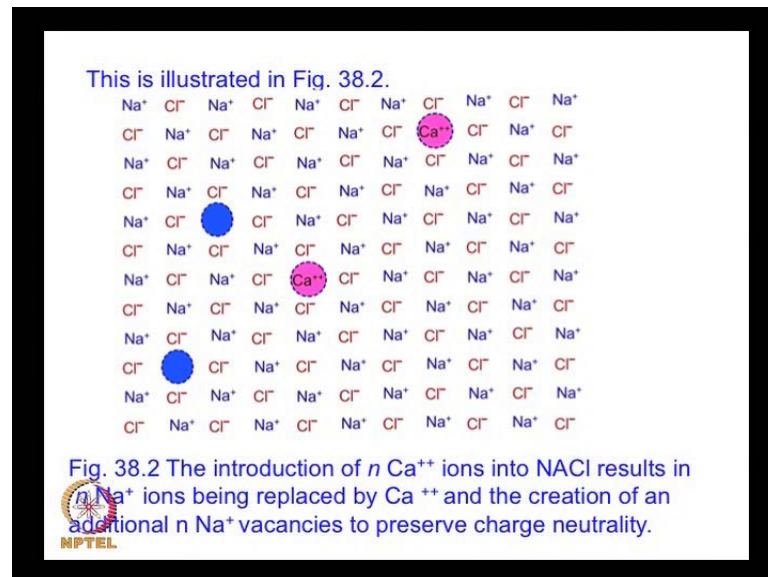
So, usually the energy involved  $E_v$  these are the order of one electron. So, substituting these at a temperature of  $E$  equal to thousand  $k$ , which is a substantially high-temperature  $N$   $10$  to the power minus  $5$ . So, a very small number, but very significant number it is one in  $10$  to the power  $5$  atoms. So, the vacancy concentration is quite appreciable. And this is necessary in order to establish thermodynamic equilibrium, and minimize the free energy to produce vacancies in an ionic crystal for example, potassium chloride.

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One method of producing vacancies in an ionic crystal, say  $\text{KCl}$ , is to add a divalent metal chloride like  $\text{CaCl}_2$  to the crystal. This is done by growing the  $\text{KCl}$  crystal with controlled amounts of  $\text{CaCl}_2$ . The divalent calcium ion ( $\text{Ca}^{2+}$ ) occupies the normal potassium ion site, and the two  $\text{Cl}^-$  ions occupy the normal chlorine ion site in the lattice. The presence of a  $\text{Ca}^{2+}$  at a positive ion site will cause an extra positive ion in the lattice. To maintain charge neutrality one positive ion vacancy (cation vacancy) will be created at the  $\text{K}^+$  site.

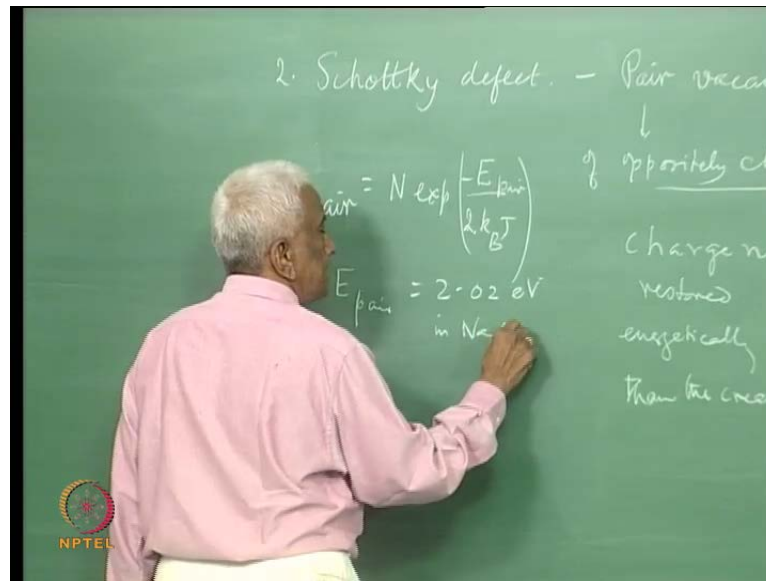
What one can do is add a divalent metal like calcium chloride to potassium chloride. So, you grow KCl crystal which controls amount of calcium chloride and divalent ion of calcium  $Ca^{2+}$  occupies a regular lattice site, which is goes into the potassium site. So, in order to establish charge neutrality we have positive ion vacancy.

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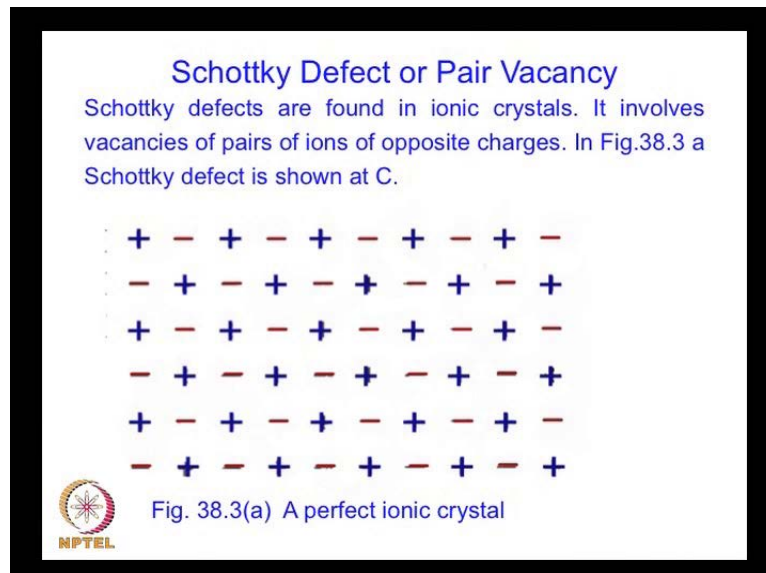
So, this is shown in the figure here how substitution calcium two plus ion for potassium ion gives results in a calcium ion vacancy in metal vacancies can be created by the so-called process of plastic deformation rapid cooling from high temperatures, which is a process known as quenching or bombarding with metal energetic particles like neutrons or irradiating metal with high energy radiation like gamma rays.

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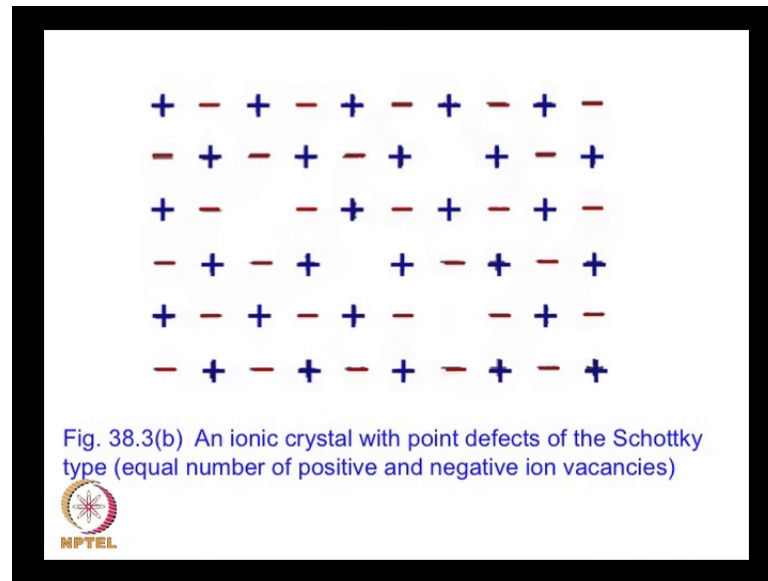
Next we consider the next kind of vacancy namely the short key defect this is the second type of point defects. So, this is a pair vacancy. So, a vacancy a pair not a single vacancy. So, these are forming ionic crystals. So, these are pairs of opposites that charged ions; obviously, this means that charge neutrality is automatically establish.

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So, energetically more favorable to create vacancy in both anion as well as cat ion site, so as to ensure the charge neutrality. So, this is obviously, caused less energy.

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So, that is illustrated in the next figure very start from a perfect ionic crystal, and then anionic crystal with a point effects of short key type, which means that there equal number of positive and negative ion vacancies.

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Formation of Schottky defect or a pair vacancy is energetically more favourable than the formation of single anion or cation vacancy, because vacant pair restores charge neutrality. The number of vacant pairs in a crystal of  $N$  ions, at temperature  $T$  is given by

$$n_{\text{pair}} \cong N \exp\left(\frac{-E_p}{2k_B T}\right) \quad (38.7)$$

where  $E_p$  is the energy required to create a vacant pair. This relation is obtained by taking the number of ways  $n$  pairs may be formed as  $\left(\frac{N!}{n!(N-n)!}\right)$

The energy of formation of a pair in NaCl is 2.02 eV.

So, this is energetically favorable more favorable than the single vacancies because of the restoration of charges neutrality. So, energetically more favorable than the creation of single vacancy which involved charge imbalance, so if you want to find the concentration of these the pair vacancies the concentration means there will be a factor

two the antirational energy is reduced half E is the energy required to create the vacancy arrive at this in case of vacancy.


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**F Centre**

A method of introducing anion vacancy in an ionic crystal is to anneal the crystal in an atmosphere of the vapour of the metal; e.g. when KCl crystal is annealed in an atmosphere of potassium vapour, anion vacancies are created. The excess potassium atom creates a potassium cation, and anion vacancy and an electron in the lattice i.e.

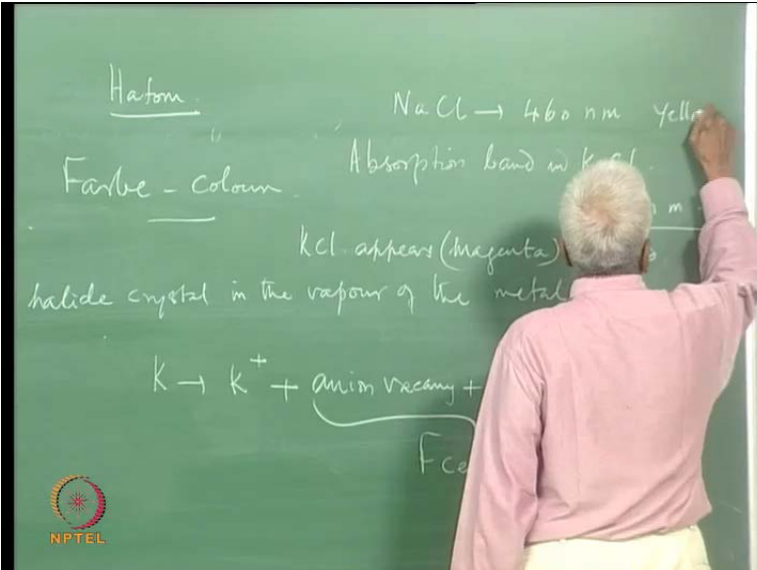
$$K \rightarrow K^{+} + \text{anion vacancy} + \text{electron}$$

The electron thus created becomes weakly bound to the anion vacancy which has an associated positive charge. This unit (electron bound to an anion vacancy) is called an F centre.



So, the energy of formation of this E pair is 2.02 electron volts in sodium chloride. Incidentally the introduction of such vacancies opens up the possibility of establishing charge neutrality in a different way other than producing pair vacancies like short key pair.

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Atom


Farbe - colour

NaCl  $\rightarrow$  460 nm yellow

Absorption band in KCl

KCl appears (magenta)

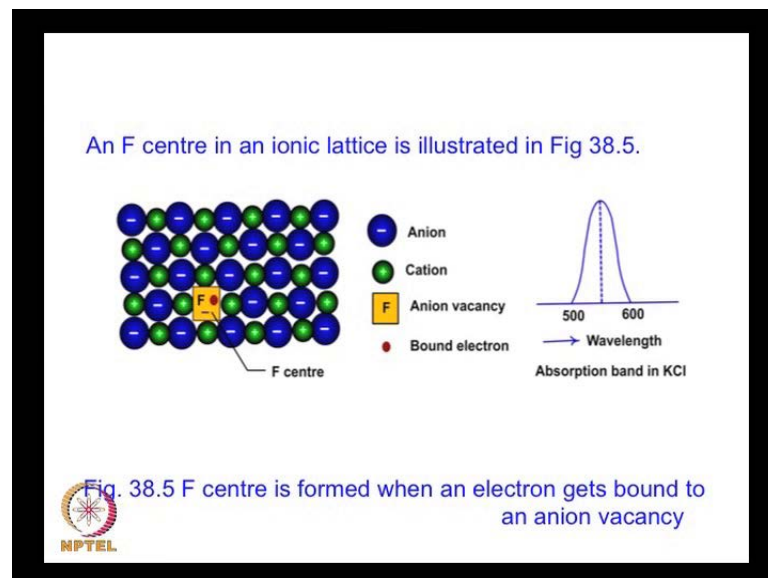
halide crystal in the vapour of the metal

$$K \rightarrow K^{+} + \text{anion vacancy} + \text{Fce}$$


This is done in so-called F centre, which is known as color centre because the production of these F centers renders an otherwise uncolored substance into color. So, it gets its color because of the characteristic optical absorption now the composition of this is that of an electron trapped in such a vacancy. So, this is an anion vacancy suppose we do this by unveiling the crystal alkali ally crystal in the vapor of metal if it is KCl the vapor of the potassium.


So, excess potassium atom creates a potassium cation and therefore, an ion vacancy under electron. So, it uses potassium plus an ion vacancy for charge neutrality plus electron. So, this is the F centre. So, the electron bound to this anion vacancy is known as the F centre F for far B which is the German word for color.

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So, the production of such a F centre's is shown in the figure shows such a F centre in an ionic lattice, and its characteristic optical absorption line is a band is also shown absorption band in KCl is also shown it occurs around 550 nanometers.

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- The  $F$  centre which has one electron bound to a positive charge behaves like a hydrogen atom and its ionization energy lies in the optical region.
- So when electromagnetic radiation (light) is incident on the ionic crystal with  $F$  centre, there is an absorption band with a peak at a particular wavelength which lies in the visible range. Because of this, the crystal appears coloured. In  $KCl$  the absorption at 565 nm (shown in Fig. 38.5).
- Due to this selective absorption in the visible range, the  $KCl$  crystal which is otherwise transparent appears coloured (magenta). When  $F$  centres are present. In sodium chloride, the absorption band lies at 460 nm and so the crystal appears yellow.


So, it behaves like a hydrogen atom because there is the electron bound to an anion vacancy. So, when electromagnetic radiation in the form of light is incident on the ionic crystal such as  $F$  centre's there is an absorption band with a peak at wavelength which is in the visible range, because of this the crystal appears color to be exact this is 565 nanometers in  $KCl$ . Because of this the  $KCl$  crystal which is otherwise transparent appears color  $KCl$  appears color as a magenta color with the introduction of this  $F$  centre's in sodium chloride the absorption band lies at  $NaCl$  these lies at four hundred sixty nanometers. So, the crystal appears yellow.

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### Other electronic centres

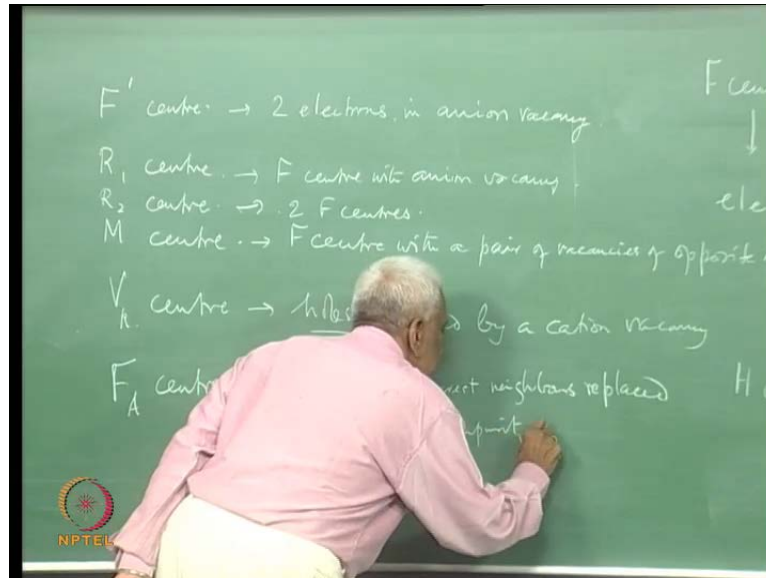
An  $F$  centre is an electron bound to an anion vacancy. There are other centres which give rise to absorption band at different wavelengths. These are:

$F''$  centre: It is an anion vacancy with two electrons bound to it. It is created when an ionic crystal which contains  $F$  centres is irradiated with radiation that is absorbed by the  $F$  centres. The radiation ionizes the  $F$  centre and the liberated electron is captured by another  $F$  centre. Thus two  $F$  centres get destroyed for the creation of one  $F''$  centre. The absorption band of the  $F''$  centres is towards the red side of the  $F$  centre band.



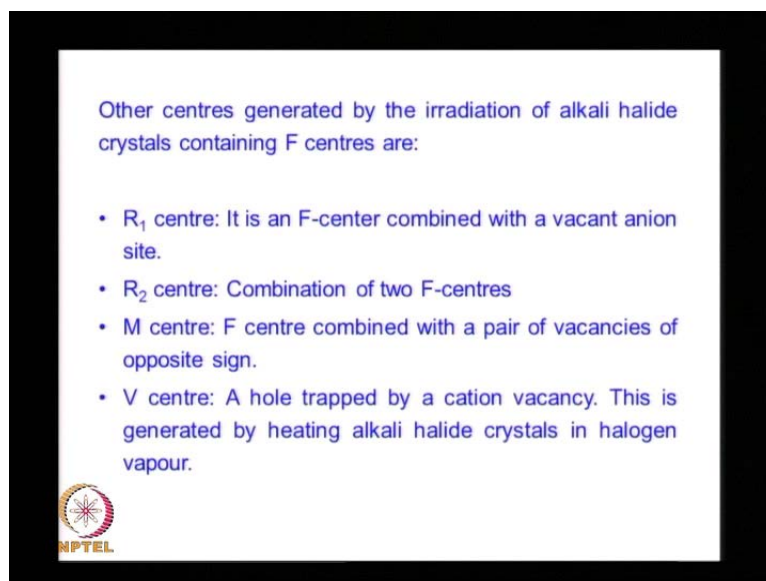
There can be other electronic centres the physics of color centres provides a value probe into the nature and dynamics of the alkaline earth halides, and fluoride all these related F prime centre.

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So, this is an ion vacancy with two electrons. So, the F – centre is one possibility then you have the R centre R one centre the M centre the M centre is S with a pair vacancies of opposite sign.

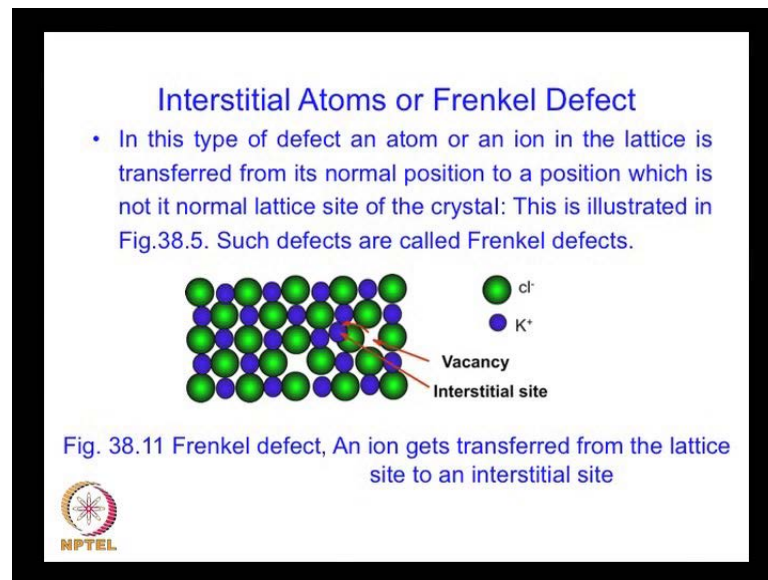
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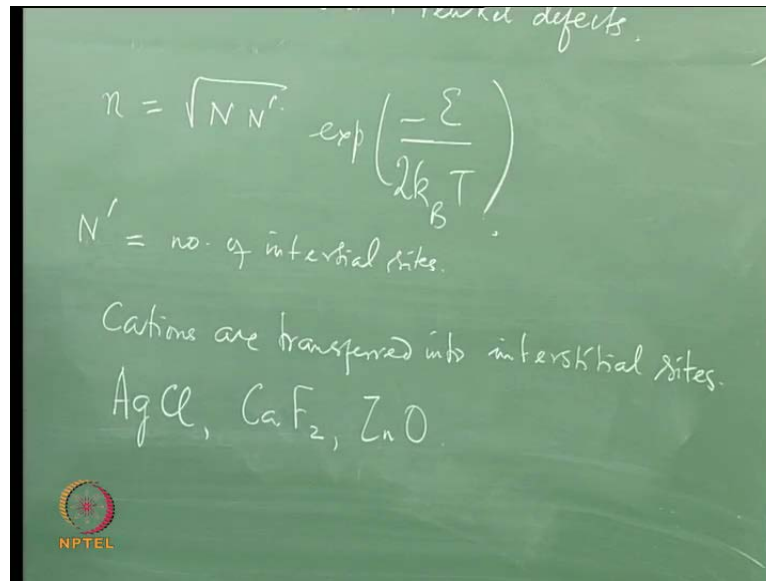
Then you also have an art to centre's here these are involved in three are one centre is F centre is combined with an ion vacancy are to centre are F centre's then you have are centre these are whole strapping cat ion vacancies the most well-known type of centre on this kind it will be k centre. So, this can be generated just by leaping alkali crystals in halogen vapor. So, the absorption spectrum of different types of centre's in KC l are shown in the next figure and the composition of different types of centre's the N centre the vk centre the h centre h centre is similar to the v k centre. But it is an interstitial type and the F a centre, in which one of these nearest neighbor positive ions surrounding a negative ion vacancy is replaced by an impurity ion one of the six near neighbors nearest neighbors replaced with an impurity ion, which we call a.

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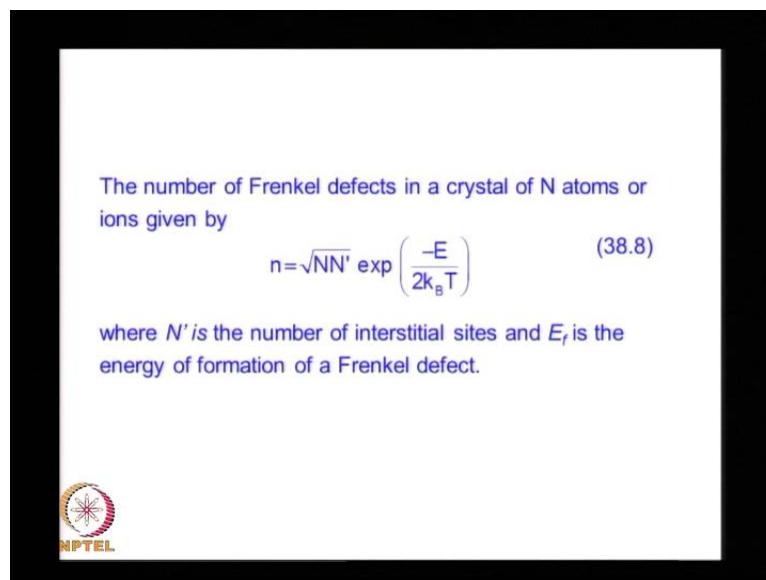
So, these are the different types of colors centers which produce a rich variety of optical absorption bands and spectra which can be used to probe the solid as well as to produce devices of different kinds for example, photo chromic glasses which are used in spectacles there made using F centre's.

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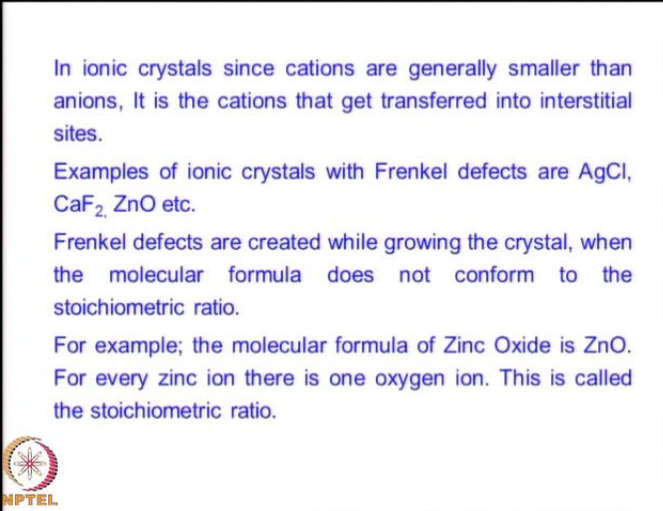
We now come to the third type known as the interstitial atom or freckled effects, this is shown in the next figure 385. And here an atom or an ion in the lattice displaced from the normal position to a position which is inside the interstitial.

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So, these are known as Frenkel defects again we can find by similar argument that the concentration equilibrium concentration Frenkel defects is given by  $\sqrt{N N'}$  exponential minus  $E$  by  $k_B T$ . Now  $N'$  is the number of interstitial sites this is because the pushing of this charge balance.

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In ionic crystals since cations are generally smaller than anions, it is the cations that get transferred into interstitial sites.

Examples of ionic crystals with Frenkel defects are AgCl, CaF<sub>2</sub>, ZnO etc.

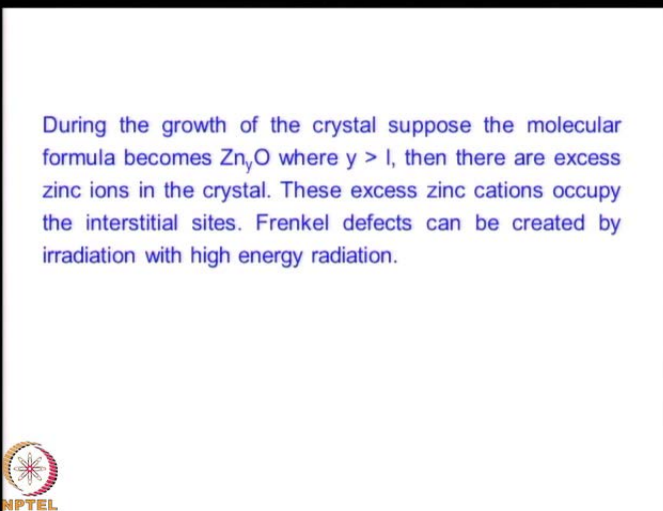
Frenkel defects are created while growing the crystal, when the molecular formula does not conform to the stoichiometric ratio.

For example; the molecular formula of Zinc Oxide is ZnO. For every zinc ion there is one oxygen ion. This is called the stoichiometric ratio.




And that is a constraint, which has to be used in conjunction with the indie minimization process of free energy. So, usually in ionic crystal cat ion are usually much smaller usually cat ions are transferred into interstitial sites. For example silver chloride silver is a very small ion g plus than calcium fluoride zing oxide these are examples of solid which have Frenkeld efects these are created by growing the crystal by the molecule formula does not not conform to this ratio. For example, inzinc oxide that these one zinc ion for every oxygen ion that this ratio during the growth of the crystal.

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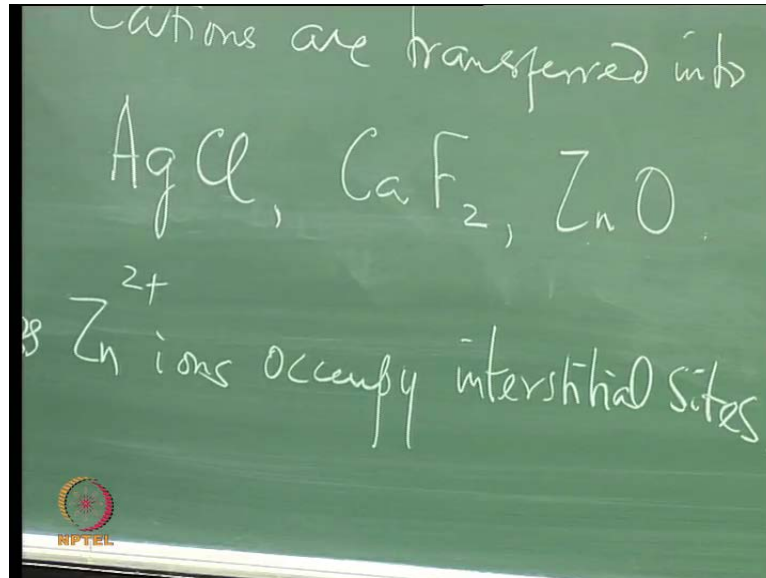


During the growth of the crystal suppose the molecular formula becomes Zn<sub>y</sub>O where  $y > 1$ , then there are excess zinc ions in the crystal. These excess zinc cations occupy the interstitial sites. Frenkel defects can be created by irradiation with high energy radiation.



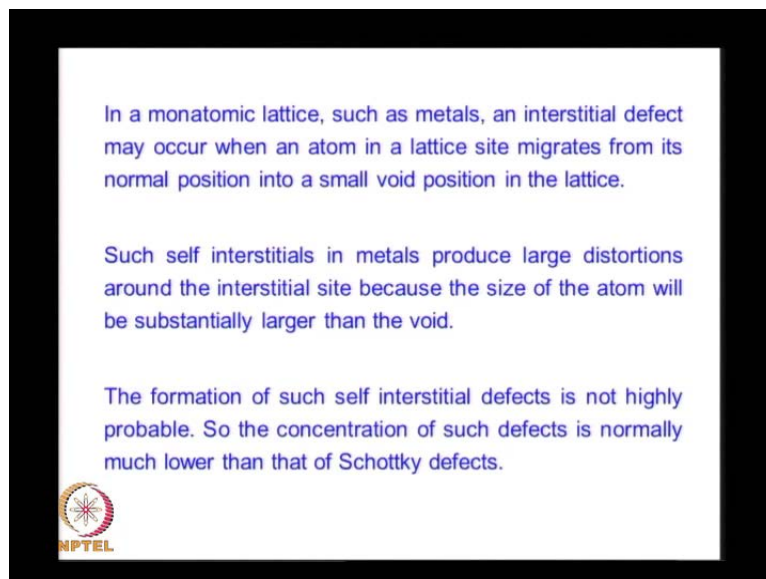
Suppose the molecule formula become  $Zn_yO$ , where  $y$  is greater than one then it is non stoichiometric this non-sky symmetry means, that there is a excess of zinc ion in the crystal.

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And these occupied the interesting excess zinc occupy interstitial sites Frenkel defects of the can also be created by bombarding with high-energy radiation in monatomic lattice.

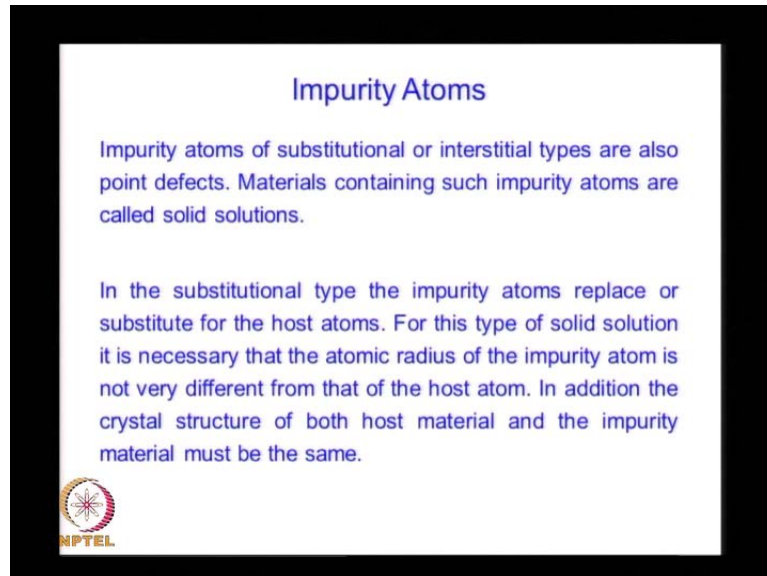
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And interstitial defect may occur when the atom in a lattice sides migrates from the normal positioning to a small white position. So, they are self interstitial producing large

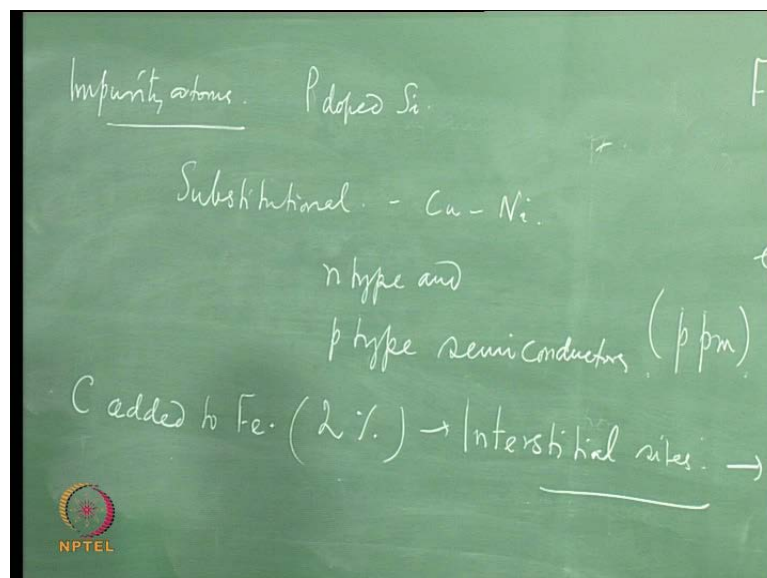
distortion surround be interstitial site because the size of the atom. So, these are not highly probable. So, usually their concentration such defects is very small.

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We can end come to the fourth category of find effect namely impurity atoms, we have already discussed them in connection with semiconductors.


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So, for example, for us doped silica on, so the pair first for us the is a pent-up valet impurity. So, doping to silly con which as for tetrahedral orbiters. So, you can have a situational impurity, which means the impurity atom simply goes into the position of the

host atoms in order to do this the atomic radii should be comparable of the impurity atoms and the holes state.


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- An example of this type of solid solution is copper-nickel. Another classic example is provided by *n-type* and *p-type* impurities added to the semiconductors, Si and Ge.
- In the interstitial type the impurity atoms occupy the voids or the interstitial sites in the host lattice.
- For metallic host lattices which have a high packing factor (FCC or HCP), the interstitial positions are relatively small. So the atomic diameter of the interstitial impurity must be much smaller than that of the host atom.

And the crystal structures of the both should be the same for example, copper nickel the copper nickel alloy and then of course, n type and p type semiconductors. So, these are standard examples of such impurities.

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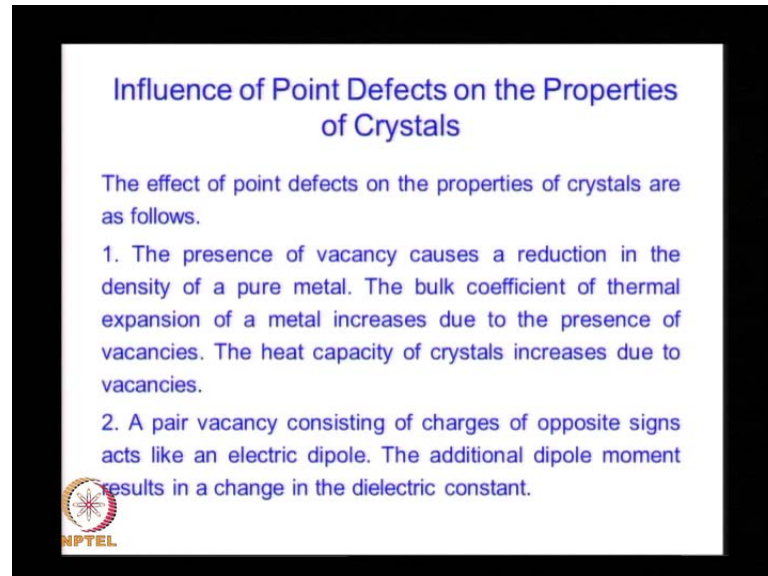


- Such interstitial atoms produce considerable distortion of the lattice around it. Normally the concentration of such impurity atoms that can be added to a metal is quite low (less than 10 %).
- An example of this type of solid solution is carbon added to iron. The maximum allowed concentration of carbon is about 2%.
- Other examples are, impurities added to ionic crystals to control their optical properties like optical absorption, birefringence, electrooptic coefficients, etc.

You can also have a situation like carbon added to iron that gives you about two percent say these are millions level, when this is done you have a interstitially sites for the purity

for this reason their composition cannot be concentration cannot exceed say two percent. So, optical absorption birefringence electro optics coefficients all this can be modified.


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**Influence of Point Defects on the Properties of Crystals**


The effect of point defects on the properties of crystals are as follows.

1. The presence of vacancy causes a reduction in the density of a pure metal. The bulk coefficient of thermal expansion of a metal increases due to the presence of vacancies. The heat capacity of crystals increases due to vacancies.
2. A pair vacancy consisting of charges of opposite signs acts like an electric dipole. The additional dipole moment results in a change in the dielectric constant.

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So, the presence of point defects on the property crystal are for example, if we have vacancy we present in the solid; that means, density will automatically get reduced. And therefore, the bulk coefficient of thermal expansion will increase due to the presence of the vacancies the heat capacity as the crystal also increases due to vacancy, if you have a pair of vacancy like a short key pair consisting a of charge of opposite signs then it acts as the electric dipole. So, this dielectric dipole moment causes the changing the dielectric constant.

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3. The presence of F-centers and other such centres affect the optical absorption properties of crystals. Crystals that are normally transparent appear coloured when colour centers are present.

4. The presence of impurities influences many properties of crystals depending on the type of impurities. For example, carbon is added to iron to improve its mechanical properties. Carbon is an interstitial impurity in iron lattice.

In semiconductors such as Si and Ge trivalent and pentavalent impurities are added as substitutional impurities to control their electrical conductivity.

And as we have already seen the presence of color centers such as F centers and other such centre aspect the optical absorption properties of crystal, and crystal that are normally plan current appear colored when color centers are present the presence of impurities for a impurity atom also modifies the behavior. For example, carbon added to ion improves the mechanical properties in semiconductors we have already seen that doping n or p type doping changes conduction property substantially. So, these are the various effects of point defects or crystal lattices. In the next lecture we will consider lying and planar defects.