

## Imperfections in Crystalline Solids

- Definitions and Classification
- Thermodynamics of Point Defects in Monoatomic Solids
- Point Defects in Ionic Crystals
- Experimental Determination of Crystal Defect Parameters
- Line Defects: Dislocations
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## Definitions and Classification

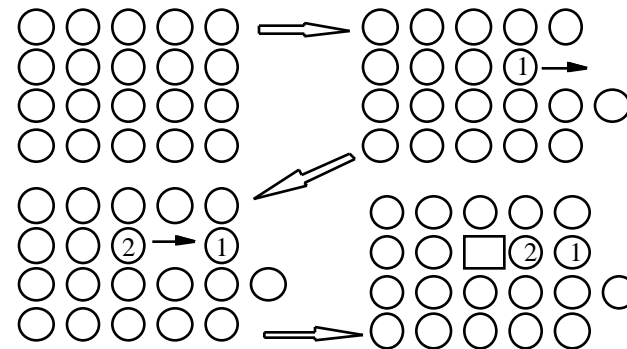
- Perfect crystals do not exist: Defects exist in crystals which result in departure from periodicity. Some defects are the result of crystal growth and handling (dislocations, grain boundaries), others are intrinsic properties of the crystalline state at non-zero (Kelvin) temperature (vacancies or interstitials).
- Various defects affect various type of physical or chemical properties of crystalline solids. It is thus extremely important to understand the origin and nature of defects in crystals.
- A useful classification of defects is on the basis of their dimensionality:
  - Dim = 0 :point defects
  - Dim = 1: line defects
  - Dim = 2: planar defects
  - Dim = 3: volume defects

## Defect Classification

- Point Defects:
  - Vacancies: Diffusion, Color Center
  - Interstitials: Mechanical Properties, Diffusion
  - Impurity Atoms: Electrical Properties
- Line Defects:
  - Dislocations: Mechanical Properties
- Planar Defects:
  - Grain Boundaries: Fabrication, Corrosion
  - Stacking Faults: Mechanical Properties
- Volume Defects:
  - Voids: Porosity, Precipitation
  - Second Phase: Mechanical and Magnetic Properties

## Thermodynamics of Point Defects in Monoatomic Solids

- Vacancies: Vacant Lattice Sites: Schottky Defects  
Mechanism of formation: Atoms pop out onto the surface (internal surface, grain boundary or dislocation) and the vacancy diffuses into the bulk of the crystal.



- Energy is required for the motion of an atom from the interior of the crystal to the surface. However, as a result of the creation of a vacancy, the entropy of the crystal increases (which is in itself would lead to a decrease in free energy). The vacancy concentration at equilibrium can then be obtained at any temperature by minimizing the free energy of the crystal with respect to the concentration of vacancies.

Let us denote  $N_L$  the number of lattice sites and  $N_V$  the number of vacancies in the crystal. The number of ways  $N_V$  vacancies can be arranged on  $N_L$  lattice sites is given by the combinatorial law and the entropy of mixing vacancies with non-vacancies is given by the Boltzmann equation:

$$S_M = k \ln \left( \frac{N_L!}{N_V!(N_L - N_V)!} \right)$$

- Application of Sterling's approximation for large values of  $N_L$  and  $N_V$  gives:

$$S_M = k \left[ N_L \ln N_L - N_V \ln N_V - (N_L - N_V) \ln (N_L - N_V) \right]$$

which can be rearranged to :

$$S_M = -k \left[ N_V \ln \frac{N_V}{N_L} + (N_L - N_V) \ln \frac{N_L - N_V}{N_L} \right]$$

The complete Helmholtz Free Energy of the System can then be written as:

$$F_V = N_V [ E_V - T S_V ] + RT S_M$$

where  $S_V$  is the change in vibrational entropy arising from the vibrational frequency spectrum around the vacancy.

Minimization of the free energy with respect to the number of vacancies leads to:

$$\frac{\partial (F_V)}{\partial N_V} = [ E_V - T S_V ] + RT \ln \frac{N_V}{N_L - N_V} = 0$$

- Since the above derivation has been carried out assuming equilibrium, we can from the above minimization condition derive the equilibrium concentration of vacancies in the crystal lattice.

$$\ln \frac{N_v}{N_L - N_v} = \ln X_v = - \frac{[E_v - T S_v]}{RT}$$

and since  $N_v \ll N_L$  then the fraction of vacancies is:

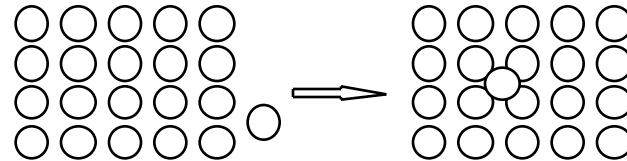
$$X_v = \exp(-F_v^0 / RT) \exp(-G_v^0 / RT)$$

which is a reasonable approximation at low pressures. The above equation is often approximated as:

$$X_v = \exp(-E_v^0 / RT)$$

which is reasonable since  $S_v$  is often low and  $H_v$  is close to  $E_v$ . It is clear that  $X_v$  increases exponentially with increasing Temperature and is zero at zero Kelvin

- Interstitial Atoms: Atoms in non-crystallographic positions  
The process of creating an interstitial is in a sense the reverse of creating a vacancy. An atom on the surface is brought into the bulk of the crystal in a non-crystallographic position.



Note that the interstitial configuration is not always that of a simple inserted atom. In many metals, the strain energy is minimized by having the neighboring atoms participate in the sharing of the strain. The calculation for the concentration of interstitials proceeds along the same line as for the vacancies.

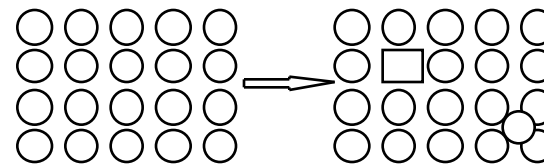
- If we denote by  $X_i$  the atomic fraction of interstitials,  $N_i$  the number of interstitials for a total number of possible interstitials  $N_{IT}$  and by  $F_i^0$ , the free energy associated with the creation of an interstitial, then the atomic fraction of interstitials at equilibrium is given by:

$$X_i = \frac{N_i}{N_{IT}} = \exp(-E_i^0 / RT)$$

Note that  $X_i$  is much larger than  $N_i/N_{IT}$  since there is considerable steric hindrance and therefore strain energy associated with the creation of an interstitial. The equilibrium concentration of interstitials is therefore usually very small. If, on the other hand, the interstitial is not the same chemical species as that making the crystal, there could be considerable concentration of interstitial (for example C in Fe in steel). Note that to be present in large concentrations, interstitial impurities (solute) have to be much smaller than the lattice atom.

- Frenkel Pairs: Creation of a Widely Separated Vacancy Interstitial Pair

The creation of a vacancy-interstitial pair can be viewed as the promotion of an atom to an interstitial position leaving a vacancy behind.



If the vacancy-interstitial pair is widely separated (few atomic distances), then it is called a Frenkel pair. When a vacancy is very close to an interstitial, they will recombine because the strain fields of opposite signs associated with each of these defects can easily cancel out by defect recombination.

- The derivation of the equilibrium atomic fraction of Frenkel pairs follows again similar lines:

$$= \frac{N_L!}{N_V!(N_L - N_V)!} \times \frac{N_{IT}!}{N_I!(N_{IT} - N_I)!}$$

Since  $N_V = N_I$ , which we will denote  $N_F$  the number of Frenkel defects, the configuration entropy will be:

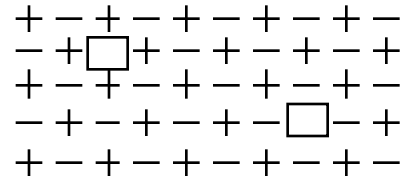
$$\frac{S_M}{k} = N_L \ln N_L - 2N \ln N - N_{IT} \ln N_{IT} - (N_L - N) \ln(N_L - N) - (N_{IT} - N) \ln(N_{IT} - N)$$

As before, we minimize the Helmholtz free energy with respect to the number of Frenkel defects, we assume that the number of Frenkel defect is much smaller than  $N_L$  and  $N_I$  and get:

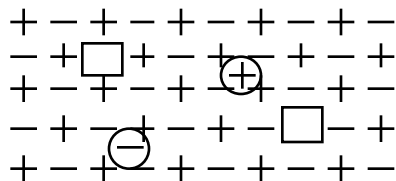
$$N_F = (N_L N_{IT})^{1/2} \exp(-F_{IV}^0 / 2 RT) \quad \text{and} \quad F_{IV}^0 = F_V^0 + F_I^0$$

- Defects in Ionic Crystals:

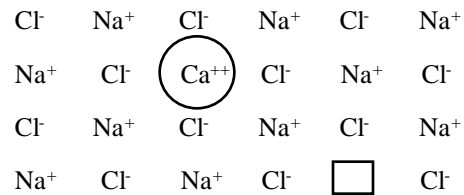
Defects in ionic crystals can be easily described using the concepts discussed above. The only differences arise from the necessity to 1) consider two kinds of atoms and 2) preserve electrical neutrality.



Schottky defects, pairs of anion and cation vacancies in an ionic crystal



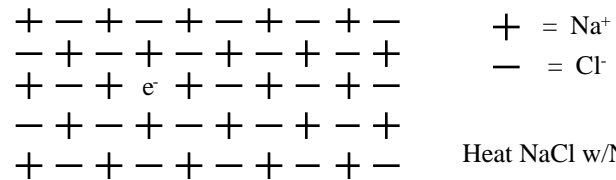
Frenkel Defects, interstitial cations and anions with corresponding vacancies in an ionic crystal



Substitution of Ca<sup>2+</sup> for Na<sup>+</sup> requires the formation of a vacancy in order to preserve electrical neutrality.

- “F” Centers: Color Centers (Color = Farbe):  
Pure alkali halide crystals are transparent throughout the visible region of the spectrum. However they can be colored by addition of impurities, the introduction of an excess metal ion (by heating the crystal in presence of metal vapors), by X-ray, g-ray, neutrons and electron bombardment, and by electrolysis.

A color center is a lattice defect that absorbs visible light.



The Sodium atom loses one electron becomes Na<sup>+</sup> and occupies a lattice site. The freed electron becomes bound to an anion lattice site.

## Experimental Determination of Crystal Defect Parameters

Experimental Vacancy Formation Enthalpies (eV):

Crystal	$H_v^0$	Crystal	$H_v^0$
Cu	1.0	NaCl	2.5
Ag	1.0	KCl	2.5
Al	0.7	KBr	2.4
Pt	1.5	KI	2.2
Pb	0.5	RbCl	2.0
W	3.3		
Na	0.4		
Fe	1.5		
Ge	2.6		

The enthalpy of vacancy formation increases with the melting temperature of the material of interest. (1 eV = 96.32 kJ)

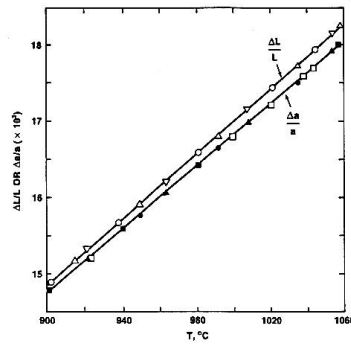
## Lattice Expansion:

- For a crystal containing  $N$  atoms and  $N_v$  equivalent point defects, the value of  $N_v/N$  and of  $\Delta L/L$  can be determined from a comparison of high temperature measurements of the macroscopic volume (measured through dilatometry) and the atomic lattice spacings determined through X-ray diffraction. As vacancies are created atoms go the crystal surface effectively increased the bulk volume of the crystal.

$$\frac{N_v}{N} = \pm 3 \frac{\Delta L}{L} - \frac{\Delta a}{a}$$

The + sign applies to the vacancy and the - sign to interstitials. The temperature dependence of  $X_v$  is exponential in  $T^{-1}$  and its slope gives the vacancy formation enthalpy,  $H_v^0$

Length expansion and lattice parameter expansion vs.  
temperature for Gold in the 900°C to 1600°C interval.  
 $L/L > a/a$  implies thermal generation of vacancies.



Simmons et al.  
Phys. Rev.  
125, 862 (1962)