INTRODUCTION

Thus far it has been tacitly assumed that perfect order exists throughout crystalline materials on an atomic scale. However, such an idealized solid does not exist; all contain large numbers of various **defects** or **imperfections.** As a matter of fact, many of the properties of materials are profoundly sensitive to deviations from crystalline perfection; the influence is not always adverse, and often specific characteristics are deliberately fashioned by the introduction of controlled amounts or numbers of particular defects. By **"crystalline defect"** is meant a lattice irregularity having one or more of its dimensions on the order of an atomic diameter. Classification of crystalline imperfections is frequently made according to geometry or dimensionality of the defect. Several different imperfections are discussed, including **point defects** (those associated with one or two atomic positions), **linear** (or one-dimensional) defects, as well as **interfacial** defects, or boundaries, which are two-dimensional. Such imperfections influence many of the characteristics of materials such as, mechanical strength, electrical properties and chemical reactions.

POINT DEFECTS

Vacancies and Self - Interstitials

The simplest point defect is a **vacancy,** or vacant lattice site, one normally occupied from which an atom is missing (Figure below). All crystalline solids contain vacancies and, in fact, it is not possible to create such a material that is free of these defects. The necessity of the existence of vacancies is explained using principles of thermodynamics; in essence, the presence of vacancies increases the entropy (i.e., the randomness) of the crystal. The equilibrium number of vacancies for a given quantity of material depends on and increases with temperature according to

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right)$$

In this expression, N is the total number of atomic sites, Q_v is the energy required for the formation of a vacancy, T is the absolute temperature in Kelvin, and k is the gas or **Boltzmann's constant.** The value of k is **(1.38×10^{-23} J/K),** or (**8.6174×10^{-5} eV/K),** depending on the units of Q_v**.** Thus, the number of vacancies increases exponentially with temperature; that is, as T in increases, so also does the expression $\exp(-Q_v/kT)$**.** For most metals, the fraction of N_v/N vacancies just below the melting temperature is on the order

of 10^{-4}; that is, one lattice site out of 10,000 will be empty. A **self-interstitial** is an atom from the crystal that is crowded into an interstitial site, a small void space that under ordinary circumstances is not occupied. This kind of defect is also represented in Figure below. In metals, a self-interstitial introduces relatively large distortions in the surrounding lattice because the atom is substantially larger than the interstitial position in which it is situated. Consequently, the formation of this defect is not highly probable, and it exists in very small concentrations, which are significantly lower than for vacancies.

Example: Calculate the equilibrium number of vacancies per cubic meter for copper at 1000^0 C. The energy for vacancy formation is 0.9 eV/atom; the atomic weight and density (at 1000^0C) for copper are 63.5 g/mol and 8.4 g/cm^3, respectively.

Solution:

$$N = \frac{N_A \rho}{A}$$

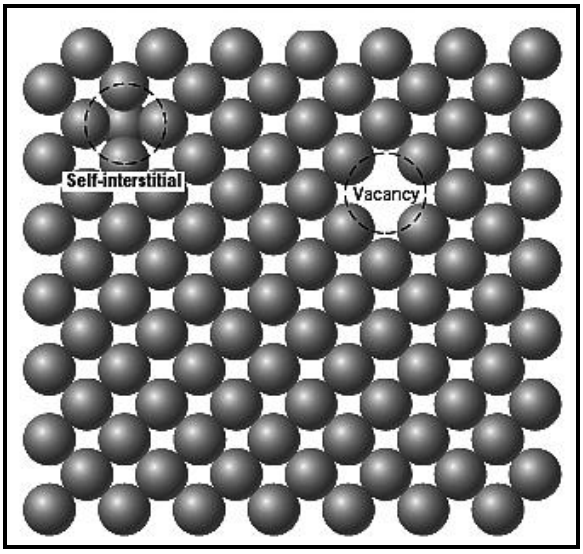
$$N = \frac{(6.023\times10^{23} atoms/mol)(8.4 g/cm^3)(10^6 cm^3/m^3)}{(63.5 g/mol)}$$

$=8\times10^{28}$ atoms/m^3

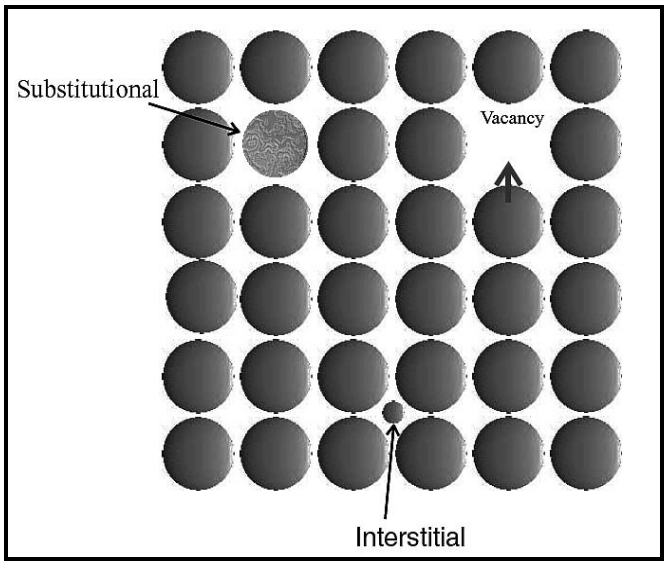
$$Nv = N\exp\left(-\frac{Qv}{kT}\right)$$

$$Nv = (8\times10^{23} atoms/m^3)\exp\left[\frac{-0.9ev}{(8.62\times10^{-5} ev/k)(1273k)}\right]$$

$= 2.2\times10^{25}$ vacancies/m^3



Impurity point defects are found in solid solutions, of which there are two types: **substitutional** and **interstitial.** For the substitutional type, solute or impurity atoms replace or substitute for the host atoms (Figure below).

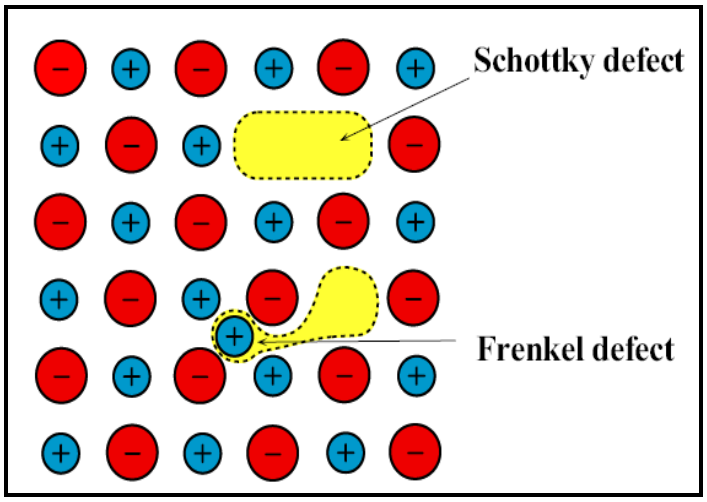


An example of a substitutional solid solution is found for copper and nickel. For interstitial solid solutions, impurity atoms fill the voids or interstices among the host atoms. For metallic materials that have relatively high atomic packing factors, these interstitial positions are relatively small. Consequently, the atomic diameter of an interstitial impurity must be substantially smaller than that of the host atoms. Normally, the maximum allowable concentration of interstitial impurity atoms is low (less than 10%). Even very small impurity atoms are ordinarily larger than the interstitial sites, and as a consequence they introduce some lattice strains on the adjacent host atoms. Carbon forms an interstitial solid solution when added to iron; the maximum concentration of carbon is about 2%.The atomic radius of the carbon atom is much less than that for iron: 0.071 nm versus 0.124 nm.

There is also the possibility of forming charged point defects in ionic crystals, and these are known as **Frenkel** and **Schottky** defects. The Frenkel defect is an interstitial of a charged atom that, when formed, creates two regions of different polarity. It is often referred to as an interstitial pair defect. The Schottky defect is also a pair defect, but it is the absence of both ions. Overall charge neutrality must be maintained for the formation of charged defects.

Frenkel defect: the atom may simply occupy a nearby interstitial position leaving a vacancy at the original lattice site, the associated vacancy and interstitial is termed a Frenkel defactes.

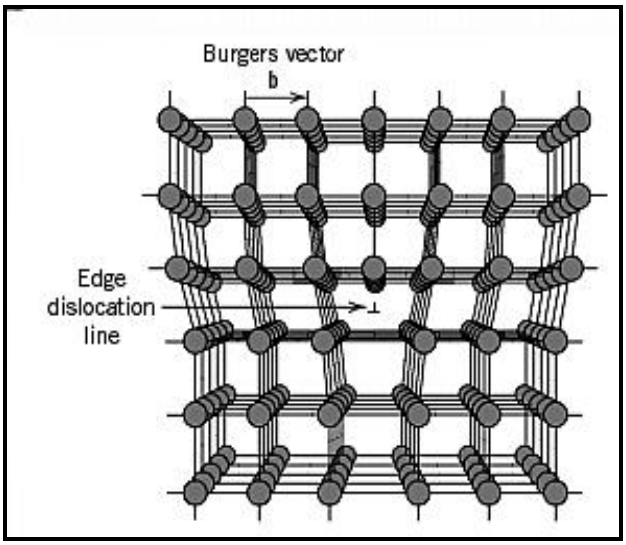
Schottky defect: the atom may migrate to the surface of the crystal, or be trapped at a line or plane defect in the crystal, vacancies of this type are referred to as Schottky defects.



Point defects can be produced in crystal in several ways:
1. By irradiation with high energy particles that when impinged on the solid ,may produce a cascade of atomic displacement and ionization.
2. By plastic deformation.
3. By quenching.
4. By increasing the temperature that increases the amplitude of vibrations of atoms, thereby increasing the probability of the formation of defects.

LINEAR DEFECTS (DISLOCATIONS)

A **dislocation** is a linear or one-dimensional defect around which some of the atoms are misaligned. One type of dislocation is represented in Figure below: an extra portion of a plane of atoms, or half-plane, the edge of which terminates within the crystal. This is termed an **edge dislocation;** it is a linear defect that centers around the line that is defined along the end of the extra half-plane of atoms. This is sometimes termed the **dislocation line,** which, for the edge dislocation is perpendicular to the plane of the page. Within the region around the dislocation line there is some localized lattice distortion. The atoms above the dislocation line are squeezed together, and those below are pulled apart; this is reflected in the slight curvature for the vertical planes of atoms as they bend around this extra half-plane. The magnitude of this distortion decreases with distance away from the dislocation line; at positions far removed, the crystal lattice is virtually perfect. Sometimes the edge dislocation is represented by the symbol ⊥ which also indicates the position of the dislocation line. An edge dislocation may also be formed by an extra half-plane of atoms that is included in the bottom portion of the crystal; its designation is a ⊤.



Another type of dislocation, called a **screw dislocation,** exists, which may be thought of as being formed by a shear stress that is applied to produce the distortion shown in (Figure a) below: the upper front region of the crystal is shifted one atomic distance to the right relative to the bottom portion. The atomic distortion associated with a screw dislocation is also linear and along a dislocation line, line *AB* in (Figure b) below. The screw dislocation derives its name from the spiral or helical path or ramp that is traced around the dislocation line by the atomic planes of atoms. Sometimes the symbol ↻ is used to designate a screw dislocation. The magnitude and direction of the lattice distortion associated with a dislocation is expressed in terms of a **Burger's vector,** denoted by a **b**. Burgers vectors are indicated in Figures above and below for edge and screw dislocations, respectively. Furthermore, the nature of a dislocation (i.e., edge or screw) is defined by the relative orientations of dislocation line and Burgers vector. For an edge, they are perpendicular, whereas for a screw, they are parallel. In addition, the Burgers vector is an element of the theory that has been developed to explain this type of deformation. Dislocations can be observed in crystalline materials using electron-microscopic techniques. In picture below, a high-magnification transmission electron micrograph, the dark lines are the dislocations. Virtually all crystalline materials contain some dislocations that were introduced during solidification, during plastic deformation, and as a consequence of thermal stresses that result from rapid cooling.