Chapter 3

Defects in Solids

There are many reasons for studying imperfections in solids. Important properties of solids depend on defects in the atomic and electronic structure of crystals. For example, it is well established that diffusion in metallic crystals depends on the presence of vacancies in the lattice. Plastic deformation in metals is known to be associated with the motion of dislocations. The electrical conductivity of many ionic solids is associated with the movements of vacancies or interstitial ions. The electrical behavior of semiconducting crystals is related to electronic imperfections. These are but a few of the practical reasons for discussing imperfections. However, it is not necessary to look only at practical considerations to justify the study of imperfections. Imperfections are interesting per se, in crystals, in oriental rugs, in postage stamps, and even in people. It has been said that a perfectly righteous person is to be respected and admired . . . but it is the sinner who makes the more intriguing study . . . and more interesting company.

This chapter treats crystal imperfections from the thermodynamic point of view. It has been noted that imperfections can be observed and analyzed in two extremes of concentration. When very dilute, imperfections are present in such low concentrations that they may be regarded as discrete entities with well-defined individual natures. This is true of point defects such as vacancies or interstitial atoms. Each such defect can be assigned properties, such as an energy and an entropy of for-

mation, that are independent of the presence of all other imperfections. An individual defect may interact with others to form simple combinations such as pairs. Again, these simple combinations may be treated as separate entities and assigned energies and entropies of their own.

At the opposite extreme of concentration, the density of defects is so high that each defect loses its individual property to the nature of the group. Surfaces, such as grain boundaries, fall into this category. These group structures may be assigned properties such as interfacial tension, that make their description in thermodynamic terms possible.

This chapter deals with the thermodynamics of point defects. The thermodynamics of surfaces is treated in Chapter 4.

3.1   STRUCTURAL POINT DEFECTS IN ELEMENTAL CRYSTALS

A missing atom in the crystal structure of an elemental crystal is a *vacancy* or a *point defect*. If the absence of an atom on a lattice site causes no changes in the rest of the crystal, we can apply in a simple way the principles learned in Section 2.6 to the case of vacancies in elemental crystals. The crystal will consist of N atoms and n vacant lattice sites (vacancies). Assume that the energy to create such a vacancy is given by E_v. There are thus two states of a lattice site to be considered:

an occupied state $E = 0$
an unoccupied state $E = E_v$

The probability of finding such an unoccupied state is related to the energy required to produce the vacancy and the temperature of the crystal (from Section 2.5, Eq 2.7) is:

$$P_v = \frac{\exp(-E_v/kT)}{Z} \tag{3.1}$$

where $Z = 1 + \exp(-E_v/kT)$

$$P_v = \frac{n}{n + N} = \frac{\exp(-E_v/kT)}{1 + \exp(-E_v/kT)} \tag{3.2}$$

$$\frac{n}{N} = \exp\left(\frac{-E_v}{kT}\right)$$

Equation 3.2 shows that at temperatures above absolute zero, elemental crystals at equilibrium contain vacancies. A typical value, such as the one for elemental aluminum, is $E_v = 0.75$ eV (72.4 kJ/mol).

Actually, the absence of an atom on a lattice site changes the vibration patterns of neighboring atoms (Figure 3.1). We must therefore take into account not only the energy (or enthalpy) required to produce a vacancy, but also the entropy changes in
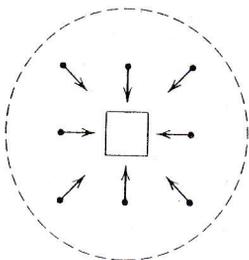
Figure 3.1 Effects of vacancy on nearest neighbors: all are ascribed to the vacancy.

the area surrounding that vacancy. At equilibrium, the Gibbs free energy of the crystal is at a minimum with respect to the number of vacancies present at constant temperature and pressure. The molar Gibbs free energy change, ΔG between the imperfect (G_i) and perfect crystal (G_p) is

$$\Delta G = G_i - G_p = n \, \Delta \underline{H}_v - T \, \Delta \underline{S} \qquad (3.3)$$

where $\Delta \underline{H}_v$ = enthalpy of formation of a vacancy
   n = number of vacancies.

The entropy term, $\Delta \underline{S}$, can be expressed as follows:

$$\Delta \underline{S} = n \, \Delta \underline{S}_v + \Delta \underline{S}_c \qquad (3.4)$$

The total change in molar entropy $\Delta \underline{S}$ is equal to the sum of entropy change required to create the vacancy $\Delta \underline{S}_v$ and the configurational entropy $\Delta \underline{S}_c$, which is related to the uncertainty in the spatial location of the vacancy. Assuming a random distribution of vacancies, this configurational entropy term can be expressed as follows:

$$\Delta S_c = k \ln \Omega = k \ln \left(\frac{(N + n)!}{N!n!} \right) \qquad (3.5)$$

After applying the Stirling approximation, we can write an expression for $\Delta \underline{G}$:

$$\Delta \underline{G} = n \, (\Delta \underline{H}_v - T \, \Delta \underline{S}_v) - kT[(N + n) \ln(N + n) - N \ln N - n \ln n] \qquad (3.6)$$

The minimum of $\Delta \underline{G}$ as a function of the number of imperfections is:

$$\left(\frac{\partial \Delta \underline{G}}{\partial n} \right)_T = \Delta \underline{H}_v - T \, \Delta \underline{S}_v + kT \ln \left(\frac{n}{N + n} \right) = 0 \qquad (3.7)$$

Solving for the fraction of vacant sites (x_v):

$$x_v = \frac{n}{N + n} = \exp\left(\frac{\Delta S_v}{k}\right) \exp\left(\frac{-\Delta H_v}{kT}\right) \qquad (3.8)$$

In general, for imperfections,

$$x_i = A \exp\left(\frac{-\Delta H_i}{kT}\right) \qquad (3.9)$$

where $A = \theta \exp(\Delta S_v/k)$ and θ is a factor to account for variations in crystallography. Note that $x_i = n_i/N$ because $n_i \ll N$.

By taking the natural logarithm of both sides, Eq. 3.9 may also be written as follows:

$$\ln x_i = \ln A - \left(\frac{\Delta H_i}{k}\right)\left(\frac{1}{T}\right) \qquad (3.10)$$

In this form it is apparent that a graph of the natural logarithm of the defect concentration (or some quantity or property linearly dependent on it) on the ordinate, and inverse absolute temperature on the abscissa, will be a straight line with a slope equal to the negative of the enthalpy of formation of the imperfection divided by k, the Boltzmann constant (Figure 3.2).

From the foregoing analysis, we conclude that vacancies are an equilibrium feature in elemental crystals at temperatures above absolute zero. These are called *intrinsic* vacancies, because they are an inherent part of the crystal. If the only
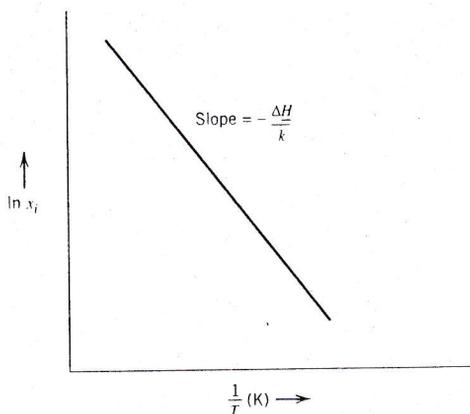
Figure 3.2 Fraction of imperfections (vacancies) as a function of inverse absolute temperature.
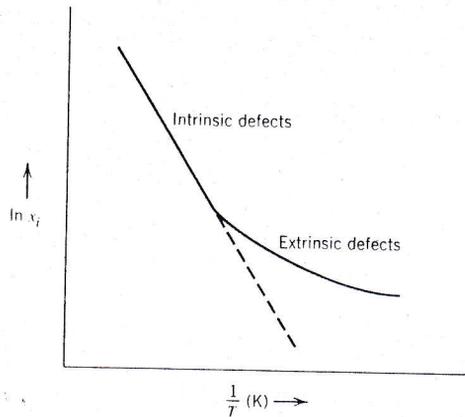
Figure 3.3 Fraction of imperfections (intrinsic and extrinsic) as a function of inverse absolute temperature.

vacancies present in a crystal are intrinsic vacancies, we will observe the linearity of $\ln x_i$ v $1/T$ shown in Figure 3.2. The concentration of vacancies may, however, be influenced by factors other than temperature.

The addition of impurities can, by distorting the lattice, create conditions near the impurity atoms that favor a vacancy concentration higher than the intrinsic concentration. The vacancies generated by such extraneous factors are called *extrinsic* vacancies. The presence of extrinsic vacancies usually manifests itself as a deviation from the linearity of $\ln x_i$ versus $1/T$ (Eq. 3.9) shown in Figure 3.2. Typically, this nonlinearity develops at lower temperatures (higher values of $1/T$), as shown in Figure 3.3. This chapter discusses several cases of extrinsic imperfections.

3.2 VACANCIES: EXPERIMENTAL VERIFICATION

In principle it should be possible to determine the values of $\Delta \underline{H}_v$ and $\Delta \underline{S}_v$ from a knowledge of the number of imperfections as a function of temperature. Unfortunately, it is difficult to measure the absolute number of imperfections. It is possible, however, to infer $\Delta \underline{H}_v$ and $\Delta \underline{S}_v$ by measuring the change in the number of imperfections with temperature. An especially novel approach to the problem was demonstrated successfully by Simmons and Balluffi (Refs. 1 and 2),[1] who asserted that

[1]Other methods have also been used to establish the temperature dependence of vacancy concentration. An early method used successfully (Refs. 3 and 4) involved quenching (rapid cooling) wires of the material being studied from high temperatures to a temperature at which the vacancies are immobile, usually below room temperature. The electrical resistivity of the wires was used as a measure of vacancy concentration. This method allows one to determine $\Delta \underline{H}_v$, but not $\Delta \underline{S}_v$. To determine both requires a measurement of the absolute number of vacancies at some temperature.

the volume of a crystal increases with increasing temperature for two reasons: the increased thermal vibration of the atoms and the creation of vacancies:

$$\Delta V = \Delta V_{\text{Th}} + \Delta V_{\text{v}} \tag{3.11}$$

The term ΔV_{Th} refers to the volume change because of increased thermal vibration of the atoms. The term ΔV_{v} refers to the volume change because of the presence of vacancies. It is equal to the number of vacancies multiplied by the volume change introduced by the presence of one vacancy, and is written as $\Delta V_{\text{v}} = n_{\text{v}} V_{\text{v}}$. To find the rate of change of ΔV_{v} with temperature at constant pressure, we substitute for n according to Eqs. 3.9 and 3.11, and differentiate with respect to temperature:

$$\left(\frac{\partial(\Delta V_{\text{v}})}{\partial T} \right)_P = \left(\frac{\partial(n_{\text{v}} V_{\text{v}})}{\partial T} \right)_P = N_A V_{\text{v}} A \exp\left[-\frac{\Delta H_{\text{v}}}{kT} \right] \frac{\Delta H_{\text{v}}}{kT^2}$$

Rearranging:

$$\frac{T^2}{V_{\text{v}}} \left[\frac{\partial \Delta V_{\text{v}}}{\partial T} \right]_P = \left[\frac{N \, \Delta H_{\text{v}} A}{k} \right] \exp\left[-\frac{\Delta H_{\text{v}}}{kT} \right] \tag{3.12}$$

Taking the natural logarithm of both sides of Eq. 3.12, we have

$$\ln\left[\frac{T^2}{V_{\text{v}}} \left(\frac{\partial \Delta V_{\text{v}}}{\partial T} \right)_P \right] = \ln\left[\frac{N \, \Delta H_{\text{v}} A}{k} \right] - \frac{\Delta H_{\text{v}}}{kT} \tag{3.13}$$

From Eq. 3.13, it is apparent that a graph of $\ln\left[\frac{T^2}{V_{\text{v}}} \left(\frac{\partial \Delta V_{\text{v}}}{\partial T} \right)_P \right]$ versus $1/T$ has a slope of $-\Delta H_{\text{v}}/k$.

The value of the term $1/V \, (\partial V_{\text{v}}/\partial T)_P$ was determined by observing the difference between the change in external dimensions of a crystal $\Delta l/l$ and the change in lattice parameter $\Delta a/a$ as the temperature of the crystal is changed. In Eq. 3.14, the first term involving Δl is associated with the total volume change of the crystal. The term involving changes in lattice parameter, $\Delta a/a$, is related to the change of volume associated only with the increased vibrations of atoms. The difference between the two is the change in volume introduced by the formation of vacancies. Because the volume is a cubic function of a linear dimension of the crystal, the $\Delta V_{\text{v}}/V$ term is three times the fractional linear changes.

$$\frac{\Delta V_{\text{v}}}{V} = 3 \left(\frac{\Delta l}{l} - \frac{\Delta a}{a} \right) \tag{3.14}$$

From these experiments Simmons and Balluffi inferred the enthalpies and entropies of formation of vacancies in aluminum, gold, and silver (Table 3.1). Based on

Table 3.1 Enthalpies and Entropies of Formation of Vacancies in Aluminum, Gold, and Silver

	ΔH_v (eV)	$\Delta S_v/k$	$\Delta n/n$ (at melting point)
Aluminum	0.75	2.2	9×10^{-4}
Gold	0.94	1.0	7.2×10^{-4}
Silver	1.09	1.5	2×10^{-4}

Source: Refs. 1 and 2.

their values, the calculated fraction of vacant lattice sites ($\Delta n/n$) at the melting point of these metals, also in Table 3.1, is shown to be almost one in a thousand. Let us use the values for silver to calculate the fraction of vacant sites at 700 K. The enthalpy and entropy values from Table 3.1 are $\Delta H_v = 1.09$ EV and $\Delta S_v/k = 1.5$.

$$\frac{n^*}{N} = \exp\left(\frac{\Delta S_v}{k}\right) \exp\left(-\frac{\Delta H_v}{kT}\right)$$

$$\frac{n^*}{N} = \exp(1.5) \exp\left(\frac{-1.09}{(8.617 \times 10^{-5})(700)}\right) = 64 \times 10^{-9}$$

The fraction of vacant lattice sites is thus about 64 parts per billion. The concentration of vacancies is the fraction of vacant sites multiplied by the number of lattice sites per unit volume, N_A/V. For silver, this calculation yields about 3.75×10^{15} vacancies per cubic centimeter at 700 K.

3.3 INTERACTIONS BETWEEN VACANCIES AND IMPURITIES

We have established that vacancies exist at equilibrium in pure, elemental crystals above absolute zero of temperature. The concentration of these intrinsic vacancies can be calculated using Eq. 3.8, if the energies and entropies of formation are known. The presence of dissolved impurity atoms in the crystal may influence the intrinsic vacancy concentration because the impurity atoms and the solvent atoms differ in size, causing vacancies to be attracted to the impurity atoms. The total concentration of vacancies would thus be modified.

To analyze this situation using statistical thermodynamics, consider that a vacancy can exist in two stable states, either bound to an impurity atom (extrinsic) or unbound (intrinsic). The total concentration of vacancies n_v is the sum of the two:

$$n_v = n_v^* + n_{1-v} \tag{3.15}$$

where n_v is total vacancy concentration (vacancies per unit volume), n_v^* is intrinsic vacancy concentration, and n_{1-v} is bound vacancy concentration.

The energy state of a vacancy depends on whether it is bound or unbound. Let

us designate the energy of an unbound vacancy as E_0 and the energy of a bound vacancy as E_{1-v}. We may, for the purpose of this analysis, assign a value of zero to the unbound energy: $E_0 = 0$. The value of E_{1-v} will be inherently negative because it is a binding energy; that is, an energy input will be required to separate the vacancy from the impurity to create an unbound vacancy. Based on Eq. 2.7, the ratio of bound to unbound vacancies is

$$\frac{n_{1-v}}{n_v^*} = \frac{g_{1-v} \exp\left(-\dfrac{E_{1-v}}{kT}\right)}{Z_{pf}}$$

where Z_{pf} (the partition function) $= g^* + g_{1v} \exp(-E_{1-v}/kT)$.

$$\frac{n_{1-v}}{n^*} = \frac{g_{1-v} \exp(-E_{1-v}/kT)}{g^* + g_{1-v} \exp(-E_{1-v}/kT)} \tag{3.16}$$

The value of the degeneracy, g_{1-v}, is the product of the impurity concentration, n_i, and Z, the coordination number in the crystal, because the vacancy may attach itself to an impurity at any of the nearest neighbor positions.[2] The degeneracy of the unbound vacancies is the number of lattice sites not nearest to impurity atoms.

$$g_{1-v} = Zn_i; \qquad g^* = N - n_i - Zn_i = N - (Z + 1)n_i$$

$$\frac{n_{1-v}}{n^*} = \frac{Zn_i \exp(-E_{1-v}/kT)}{N - (Z + 1)n_i + Zn_i \exp(-E_{1-v}/kT)}$$

Note that $N \gg (Z + 1)n_i$, and $Zn_i \exp(-E_{1-v}/kT) \ll N$ for small n_i:

$$n_{1-v} = n_v^* \frac{n_i}{N} Z \exp\left(-\frac{E_{1-v}}{kT}\right) \tag{3.17}$$

Substituting in Eq. 3.15, we write

$$\frac{n_v}{n_v^*} = 1 + \frac{n_i}{N} Z \exp\left(-\frac{E_{1-v}}{kT}\right) \tag{3.18}$$

To learn how important the extrinsic concentration can be, let us estimate some of the terms in Eq. 3.18. Let us take silver at 700 K once again as an example. Our calculation in Section 3.2 tells us that vacancies in silver are present at about 64

---

[2] The common notation for the coordination number is usually the letter Z, which we have used to signify the partition function. To avoid confusion, the notation Z_{pf} was used in this section for the partition function.

parts per billion at this temperature. It is difficult to reduce impurities in silver (n_i) to this level. A typical impurity fraction is 10^{-3}, or 0.1%. At this level, assuming a reasonable binding energy ($E_{1-v} = -0.1$ eV), and a coordination number of 12, the ratio of total vacancies to intrinsic vacancies[3] is:

$$\frac{n_v}{n^*} = 1 + 10^{-3}(12)\left(\exp\left[\frac{0.1}{(8.617 \times 10^{-5})(700)}\right]\right)$$

$$\frac{n_v}{n^*} = 1.06$$

At a 1% impurity level, this ratio rises to 1.63. This leads us to the conclusion that impurities can have an effect on vacancy concentration. Based on Eq. 3.18, this effect becomes even more important at lower temperatures.

3.4   INTERACTION BETWEEN IMPERFECTIONS AND IMPURITIES

In Section 3.3 we analyzed the effect of dissolved impurity atoms on the equilibrium concentration of point defects in a crystal, based on the formation of impurity–vacancy clusters. If there is a tendency for impurity atoms and crystal imperfections to form clusters, we should expect structural imperfections, such as dislocations, to attract and bind impurity atoms in a crystal. An interesting example of this binding is to be found in iron–carbon (steel) alloys. An accepted explanation for the "yield point" in steel is based on the binding between dislocations and solutes that occupy interstitial positions in the iron lattice, such as carbon atoms. Plastic deformation in a crystalline solid occurs when dislocations move under applied stress. In iron–carbon alloys, the stress required to start the movement of dislocations is higher than the stress required to keep them moving, giving rise to a distinct yield point (Ref. 5). The binding between dislocations and carbon atoms causes this phenomenon. The shear stress required to break the dislocation away from the relatively immobile carbon atoms is greater than the shear stress required to keep them moving. Based on reasoning similar to that used to derive Eq. 3.18, there should be fewer atoms bound to the imperfections as the temperature is increased. Thus, the yield point phenomenon should become less pronounced at higher temperatures. This is, indeed, what is observed in the iron–carbon system. At temperatures above 700°C the yield point essentially disappears.

To deal with the effect of binding of interstitial impurities to dislocations, let us adopt the same type of notation we used in Section 3.3. We can write:

$$\frac{n_{N\perp}}{n_N^*} = \frac{g_{N\perp}\exp(-E_{N\perp}/kT)}{g_N + g_{N\perp}\exp(-E_{N\perp}/kT)} \tag{3.19}$$

---

[3]The Boltzmann constant is 8.617×10^{-5} eV/K.

where n_N^* = number of intrinsic nitrogen atoms in iron per cubic centimeter (intrinsic solubility)

$n_{N\perp}$ = number of nitrogen atoms bound to dislocations

g_N = number of lattice positions available to dissolved nitrogen atoms

$g_{N\perp}$ = number of dislocation positions available to dissolved nitrogen atoms

$E_{N\perp}$ = interaction energy of dissolved nitrogen and dislocations relative to dissolved nitrogen in lattice (negative quantity)

Note that we have assigned an energy of zero to the dissolved nitrogen in a normal position (interstitial). If we can assume that $g_N \gg g_{N\perp}$, Eq. 3.19 becomes

$$\frac{n_{N\perp}}{n_N^*} = \frac{g_{N\perp} \exp(-E_{N\perp}/kT)}{g_N} \tag{3.20}$$

The total number of nitrogen atoms dissolved n_T is the sum of n_N^* and $n_{N\perp}$.

$$n_T = n_N^* + n_{N\perp} = n_N^* \left(1 + \frac{g_{N\perp} \exp(-E_{N\perp}/kT)}{g_N} \right) \tag{3.21}$$

It is apparent from Eq. 3.21 that the measured solubility of nitrogen in iron is a function of the dislocation concentration if the interaction energy $E_{N\perp}$ is not zero. Let us estimate the magnitude of the effect. Interaction energies $E_{N\perp}$, are about -0.3 eV. If a sample is severely cold-worked (rolled), dislocation densities up to 5×10^{12} cm/cm^3 can be reached. For iron, the number of interstitial positions per cubic centimeter is 8.4×10^{22}. The number of atoms per centimeter is the cube root of 8.4×10^{22}, or 4.3×10^7. Assuming, for simplicity, that we are dealing with edge dislocations, the number of dislocation positions that can occupy a nitrogen atom is the product of the dislocation density and 4.3×10^7, or 2.15×10^{20}. If we substitute these values in Eq. 3.21 at 700 K (427°C), the enhancement of observed solubility is about 37%. This effect should be observable, and, in fact, was observed by Darken (Ref. 5).

Darken conducted his experiments by equilibrating samples of iron with a mixture of ammonia and hydrogen at about 450°C. By controlling the ratio of ammonia to hydrogen, he fixed the thermodynamic activity of nitrogen, because the equilibrium constant K_a is determined by the temperature:

$$NH_3 = \tfrac{3}{2}H_2 + \underline{N} \tag{3.22}$$

$$K_a = a_{\underline{N}} \frac{P_{H_2}^{3/2}}{P_{NH_3}}$$

where underscored N indicates dissolved nitrogen.

The number of dislocations was varied by cold working the samples to different levels. The greater the degree of cold work, the higher the dislocation concentration.
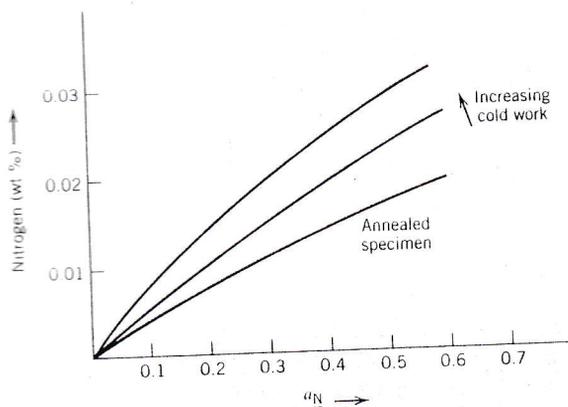
Figure 3.4 Nitrogen dissolved in iron as a function of activity of nitrogen and cold work (imperfections) in iron.

After equilibrating the iron samples with the gas of controlled nitrogen activity, Darken found higher nitrogen solubility in samples with greater cold work (i.e., the ones with higher dislocation densities). His observations are shown in Figure 3.4.

3.5   ELECTRONIC DEFECTS

Solid materials can, in broad terms, be divided into three classes with respect to their ability to conduct electrical charges: metals, semiconductors, and insulators. Metals have a high mobile carrier (electron) concentration, on the order of 10^{22} per cubic centimeter. At the other end of the scale, insulators have very few mobile charge carriers—on the order of one per cubic centimeter. The behavior of electrons in metals is discussed in texts on metal physics (see, e.g., Refs. 6 and 7). The conductivity of insulators is not discussed because, by the nature of the devices, this property cannot be varied significantly. Semiconductors are particularly interesting because their conductivity can be varied by changing the environment in which they exist. They are, thus, useful as sensors.

Intrinsic semiconductors are characterized by an energy gap (band gap) between electrons in their valence bands and allowed states in their conduction bands (Figure 3.5). To become active, in the sense of conduction, electrons must jump across the energy gap into the conduction band. When they do, they leave behind holes in the valence band. Both electrons and holes can participate in the conduction of electrical charge. Semiconductors can have a range of carrier concentrations, but for comparison with insulators and metals we can think of them as having on the order of 10^{10} mobile carriers per cubic centimeter. They are useful in electrical devices, such as transistors, or, in the case of ionic solids, as sensors, because the number of carriers changes with temperature or with the chemical nature of the atmosphere in equilibrium with the solid. In this section, we establish the relationship between charge
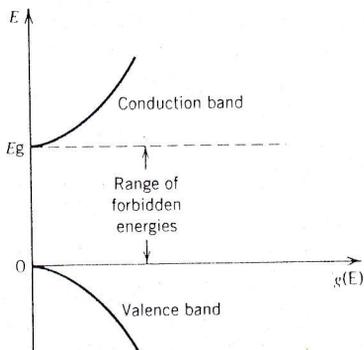
Figure 3.5 Plot of density of states $g(E)$ versus E for conduction electrons and holes in a semiconductor.

carriers in pure elemental crystals (electrons and holes) as a function of temperature and energy gap of the solid. A later section treats the effect of atmosphere.

If the two states for electrons, at the top of the valence band and at the bottom of the conduction band, had no limits as to their occupancy, calculating the probability of finding an electron at E_g relative to $E = 0$ (top of the valence band) would be a straightforward application of Boltzmann statistics (Eq. 2.7). The situation is more complicated, however, because the Pauli exclusion principle applies. Only one electron may occupy each quantum state in the crystal, taking all the quantum numbers into account, including the spins. We must therefore use the Fermi–Dirac statistics (Section 2.11). The number of electrons in the conduction band N_c is, based on Eq. 2.25:

$$N_c = \int_{E_g}^{\infty} g(E) \left[1 + \exp\left(\frac{E - \mu}{kT}\right) \right]^{-1} dE \qquad (3.23)$$

where μ is the Fermi level in the crystal, E_F, and $g(E)$ is the density of states between energy levels E and E + dE.

The density of states for the electrons in the conduction band may be derived using the same technique we used to determine the density of states for an ideal gas, that is, from the "quantum particle in a box" model. Taking into account the two spin states that may exist at each energy level, the result for electrons is

$$g(E) = 4\pi \left(\frac{2m_c^*}{h^2}\right)^{3/2} (E - E_g)^{1/2}$$

$$g(E) = C_e(E - E_g)^{1/2} \qquad (3.24)$$

where $C_e = 4\pi(2m_e^*/h^2)^{3/2}$ and m_e^* is the effective mass of an electron in the crystal.

For holes in the valence band, a similar approach yields:

$$g(E) = 4\pi \left(\frac{2m_h^*}{h^2}\right)^{3/2} (-E)^{1/2}$$

$$g(E) = C_h(-E)^{1/2}$$

(3.25)

where m_h^* is the effective mass of a ''hole'' in the valence band.

Because the Fermi level lies in the forbidden band, and its distance from the band edge is large compared with kT (which is equal to about 0.025 eV at room temperature), we may approximate the Fermi function as follows:

$$1 + \exp\left(\frac{E - E_F}{kT}\right) \approx \exp\left(\frac{E - E_F}{kT}\right)$$

(3.26)

because $(E - E_F) \gg kT$.

Substituting Eqs. 3.26 and 3.24 in 3.23 yields:

$$N_c = C_e \int_{E_g}^{\infty} (E - E_g)^{1/2} \exp\left[-\frac{(E - E_F)}{kT}\right] dE$$

(3.27)

If we let $x = (E - E_g)/kT$, Eq. 3.27 becomes

$$N_c = C_e(kT)^{3/2} \exp\left[-\frac{(E_g - E_F)}{kT}\right] \int_0^{\infty} x^{1/2} e^{-x} dx$$

For the definite integral, we write

$$\int_0^{\infty} x^{1/2} e^{-x} dx = \tfrac{1}{2} \sqrt{\pi}$$

hence:

$$N_c = 2 \left(2\pi \frac{m_e^* kT}{h^2}\right)^{3/2} \exp\left[-\frac{E_g - E_F}{kT}\right]$$

(3.28)

By a similar process, the number of holes present in the valence band is,

$$N_h = 2 \left(2\pi \frac{m_h^* kT}{h^2}\right)^{3/2} \exp\left(-\frac{E_F}{kT}\right)$$

(3.29)

If we are dealing with an intrinsic semiconductor—that is, one in which there is

a hole left behind for every electron in the conduction band (no donor or acceptor impurities)—then,[4]

$$N_c = N_h \qquad (3.30)$$

Substituting Eqs. 3.28 and 3.29 in Eq. 3.30:

$$E_F = \frac{E_g}{2} + \frac{3}{4} kT \ln \frac{m_h^*}{m_c^*} \qquad (3.31)$$

Since kT is small, and the values of m_c^* and m_h^* are not greatly different, the Fermi level may be considered to be in the middle of the energy gap for intrinsic semiconductors.

If we think of the formation of conduction electrons and holes as a chemical reaction, we can write:

$$\text{null} = N_c + N_h \qquad (3.32)$$

The product of N_c and N_h is a function of temperature, much as the equilibrium constant is, and has a value:

$$N_c N_h = 4 \left(\frac{2\pi k}{h^2}\right)^3 (m_c^* m_h^*)^{3/2} T^3 \exp\left(-\frac{E_g}{kT}\right) \qquad (3.33)$$

It is interesting to note that the term for the Fermi level, E_F, drops out of Eq. 3.33, and the product of N_c and N_h depends only on temperature and the energy gap, E_g. In contrast to a simple, two-energy-level situation in which the Boltzmann distribution (Eq. 2.7) would apply, the product of the number of electrons and holes is in this case a function of E_g/kT, but also a function of T^3.

3.6   DEFECTS IN IONIC COMPOUNDS

The preceding sections dealt with defects in elemental crystals, where the atoms were all of the same species. Ionic compounds have a minimum of two elements, an electropositive element, designated by M, and an electronegative element, designated by X. Vacancies may occur on either the electropositive or the electronegative lattice. Additionally, both the electropositive and the electronegative elements may take interstitial positions in the lattice. Each type of defect is discussed in the sections that follow.

---

[4]In many publications, N_c, the number of electrons in the conduction band, is written simply as "n." The number of holes N_h is written as "p," referring to a positively charged conduction species.

Table 3.2 Summary of Kroger–Vink Notation

Symbol	Definition
M	Atom of electropositive element
X	Atom of electronegative element
M_M	M atom on M site (sometimes denoted as M_M^x)
N_M	N atom on M site
V_M	Vacancy on M site
M_i	M atom on interstitial site
$M_i^{\cdot}$	Positively charged M ion on interstitial site (singly ionized)
$M_i^{\cdot\cdot}$	Positively charged M ion on interstitial site (doubly ionized)
V_i'	Negatively charged X ion on interstitial site (singly ionized)
$V_X^{\cdot}$	Positively charged vacancy (relative to perfect lattice) on X site
V_M'	Negatively charged vacancy (relative to perfect lattice) on M site

Source: Ref. 8.

For the purposes of our discussion, we will adopt the Kroger–Vink notation (Ref. 8) to represent these imperfections (Table 3.2). An easy way (Ref. 9) to understand the notation is to consider that each point defect is represented by a three-part symbol, X_Y^Z, where

X represents *what* is on the site (V for a vacancy and an elemental notation if the site is occupied by an element)

Y represents the *type* of site occupied by X (i for an interstitial site, or, for a lattice site, the symbol for the element usually occupying that lattice site)

Z represents the *charge* relative to the normal ionic charge on the site Y [positive charges are represented by dots ($\cdot$ or $\cdot\cdot$), and negative charges by primes (' or "); a lowercase letter x is sometimes used to denote a neutral atom].

In silver chloride, AgCl, an interstitial silver ion is represented as $Ag_i^{\cdot}$. A vacancy on the silver lattice is represented as V_{Ag}'.

Equations describing defect formation or annihilation must adhere to the following principles:

1. Conservation of mass
2. Conservation of charge (electroneutrality)
3. A fixed ratio of M and X sites according to the compound being studied

3.7 FRENKEL DEFECTS

One type of defect in an ionic solid is formed when an ion normally found on one of the lattice positions lies in an interstitial position in the structure, and a lattice position corresponding to that element is vacant. This is called a *Frenkel defect*. The

formation of a Frenkel defect by an electropositive element (M) may be expressed as a chemical equation:

$$MX = M_{(1-\delta)}X + \delta V_M + \delta M_i \qquad (3.34)$$
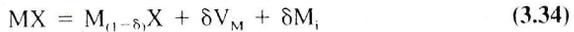
In the Kroger–Vink notation, which we will use, this is written as follows:

$$M_M = M_i^{\cdot} + V_M' \qquad (3.35)$$

We have assumed that the interstitial M atom is ionized with a charge of +1. The vacancy has a charge of −1 relative to the perfect lattice. If we think of the change expressed in Eq. 3.35 as a chemical reaction, we can write an equilibrium constant for it:

$$K_1 = \frac{a_{M_i^{\cdot}} a_{V_M'}}{a_{M_M}} \qquad (3.36)$$

The activity of the material M (a_{M_M}) is very close to unity because only small quantities of defects are formed. Using the infinitely dilute solution as the standard state for the imperfections makes their activities equal to their concentrations[5]:

$$K_1 = [M_i^{\cdot}][V_M'] \qquad (3.37)$$

To describe the concentration of these imperfections as a function of temperature, we follow the same procedure we used for elemental crystals, with the complication that we must account for the configurational entropy ($\Delta \underline{S}_c$) of both the vacancies and the interstitials. There is uncertainty concerning the position of the vacancies and also uncertainty related to the position of the interstitials. If we assume that the locations of the vacancies and the interstitials are random and independent of one another, we can write

$$\Delta \underline{S}_c = k \ln \left[\frac{(N + n_v)!}{N! n_v!} \frac{(N + n_i)!}{N! n_i!} \right] \qquad (3.38)$$

where n_v = number of vacancies
n_i = number of interstitials

Proceeding as in Section 3.1, we obtain:

$$\left(\frac{n_v}{N + n_v} \right) \cdot \left(\frac{n_i}{N + n_i} \right) = \exp \left(\frac{\Delta S_f}{k} \right) \exp \left(-\frac{\Delta H_f}{kT} \right) \qquad (3.39)$$

---

[5]Square brackets [ ] denote the concentration of the species in the brackets.

but

$$n_v \ll N; \qquad n_i \ll N; \qquad [V'_M] = \frac{n_v}{V}; \qquad [M_i^{\cdot}] = \frac{n_i}{V}$$

For one mole of crystal:

$$[V'_M][M_i^{\cdot}] = \frac{N_A^2}{\underline{V}^2} \exp\left(\frac{\Delta \underline{S}_f}{k}\right) \exp\left(-\frac{\Delta \underline{H}_f}{kT}\right) \qquad (3.40)$$

The Frenkel defect concentration, [F] is equal to the concentration of either the interstitials $[X_i]$ or the vacancies [V], if the two are equal, or to the square root of their product:

$$[F] = ([V'_M][M_i^{\cdot}])^{1/2} = \frac{N_A}{\underline{V}} \exp\left(\frac{\Delta \underline{S}_f}{2k}\right) \exp\left(-\frac{\Delta \underline{H}_f}{2kT}\right) \qquad (3.41)$$

This term, [F], is called the intrinsic Frenkel defect concentration and is related to the entropy and enthalpy of formation of the defect.

The preceding illustration was based on Frenkel defect formation by the electropositive (M) elements. The same can also occur for the electronegative (X) elements.

3.8 SCHOTTKY–WAGNER DEFECTS

A defect in an ionic crystal may be created by having an electrical-charge-equivalent number of vacancies created on the electropositive and electronegative lattices. If the electropositive and electronegative elements have the same valence, there will be the same number of vacancies on each lattice. If the valence of the two elements is different, the number of vacancies is inversely proportional to their valence states. In the case of similar valence this can be expressed as a chemical equation as follows (the term ''null'' represents the defect-free lattice):

$$\text{null} = V_X^{\cdot} + V_M' \qquad (3.42)$$

In terms of an equilibrium constant, this can be written as follows:

$$K_2 = [V_X^{\cdot}][V_M'] \qquad (3.43)$$

Note that the term $[M_M']$ appears both in Eqs. 3.37 and 3.43. Both Frenkel and Schottky–Wagner defects may be present in the same crystal. Chemical equilibrium requires that both equilibria be satisfied in addition to the condition of stoichiometry, which in this case corresponds to electroneutrality among the charged species. Because of these conditions, we may write:

$$[V'_M] = [M^{\cdot}_i] + [V^{\cdot}_X] \tag{3.44}$$

$$[M^{\cdot}_i] = \frac{K_1}{[V'_M]} \; ; \; [V^{\cdot}_X] = \frac{K_2}{[V'_M]}$$

$$[V'_M]^2 = K_1 + K_2 \tag{3.45}$$

$$[V'_M] = (K_1 + K_2)^{1/2}$$

Thus the concentration of vacancies on the electropositive lattice depends on the presence of both Frenkel and Schottky–Wagner defects.

3.9   INTERACTIONS AMONG DEFECTS

In Section 3.7 we demonstrated that the concentrations of Frenkel and Schottky–Wagner defects are interdependent. This interdependence of defect concentrations also holds for a wide variety of other defects. In this section we discuss a useful way of representing these relationships in diagrammatic form. In the literature of the field, the diagrams are called either Brouwer diagrams or Kroger–Vink diagrams (Refs. 8 and 10).

Take as an example the case of an ionic solid, represented as MX, which is exposed to the vapor of the metal M at various pressures. Let us assume that the metal vapor interacts with the MX crystal to form interstitial ions and electrons, which we will label n':

$$M(g) = M^{\cdot}_i + n'$$
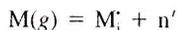
The equilibrium among the species in the reaction is represented by

$$K_F = \frac{[n'][M^{\cdot}_i]}{P_M} \tag{3.46}$$

We note that there are also charged vacancies on the M sublattice, and we must accommodate to the Frenkel defect equilibrium:

$$K'_F = [M^{\cdot}_i][V'_M] \tag{3.47}$$

In addition, there is an equilibrium between free electrons (n') and holes (p'):

$$K_i = [n'][p^{\cdot}] \tag{3.48}$$

Electroneutrality of the crystal imposes the following condition:

$$[n'] + [V'_M] = [p^{\cdot}] + [M^{\cdot}_i] \tag{3.49}$$

If we take the natural logarithms of the terms in Eqs. 3.46, 3.47, and 3.48, we obtain:

$$\ln K_F = \ln[M_i^{\cdot}] + \ln[n'] - \ln P_M \qquad (3.50)$$

$$\ln K_F' = \ln[M_i^{\cdot}] + \ln[V_M'] \qquad (3.51)$$

$$\ln K_i = \ln[n'] + \ln[p^{\cdot}] \qquad (3.52)$$

The construction of a Brouwer (or Kroger–Vink) diagram proceeds by noting that certain approximations may be made in different ranges of metal vapor pressure values. For example, in a low metal pressure range we may assume that the concentrations of interstitial cations and holes predominate. Based on the condition of electroneutrality (Eq. 3.49) the concentrations of the two are equal:

$$[p^{\cdot}] = [V_M'] \qquad (3.53)$$

As the pressure in the metal vapor increases, we enter a region of stoichiometry in which the concentrations of interstitial cations and negatively charged vacancies are equal (Frenkel defect):
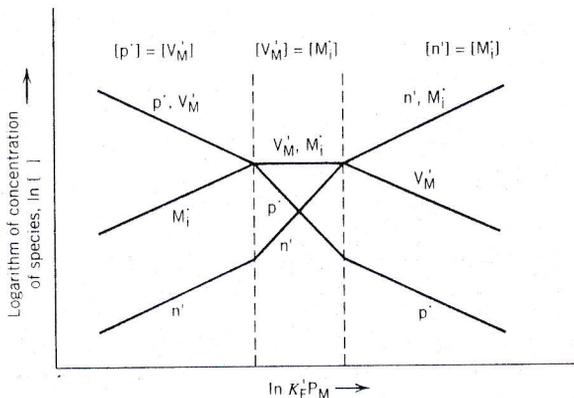
$$[V_M'] = [M_i^{\cdot}] \qquad (3.54)$$

Finally, as the pressure increases, we enter a region where the concentration of cation interstitials is equal to the concentration of free electrons:

$$[n'] = [M_i^{\cdot}] \qquad (3.55)$$
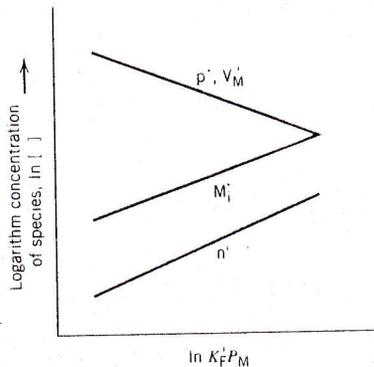
Figure 3.6 Concentration of charged species in MX exposed to M(g) as a function of metal vapor pressure.

Figure 3.7 Concentration of various species in MX exposed to M(g) as a function of metal vapor pressure.

Treating the case represented by Eq. 3.53, we can write Eq. 3.50 as follows:

$$\ln P_M = \ln[M_i^{\cdot}] + \ln[n'] - \ln K_F \qquad (3.50')$$

Combining Eqs. 3.51 and 3.52 yields:

$$\ln \left(\frac{K_F'}{K_i}\right) = \ln[M_i^{\cdot}] - \ln[n'] \qquad (3.56)$$

Combining the results of Eqs. 3.50′ and 3.56 yields:

$$\ln P_M = 2\ln[M_i^{\cdot}] - \ln \left(\frac{K_F' K_F}{K_i}\right) \qquad (3.57)$$

These relationships are shown schematically in Figure 3.6. Note that on the right-hand side of Figure 3.6 the concentration of cation interstitials becomes equal to the concentration of cation vacancies, and we enter the pressure region dominated by Frenkel defects. A further increase in gaseous metal vapor pressure moves us into the region dominated by free electrons and cation interstitials. The concentrations of the various species involved are shown schematically in Figure 3.7.

3.10 INTRINSIC AND EXTRINSIC DEFECTS IN IONIC CRYSTALS

Vacancies in ionic crystals exist at equilibrium at temperatures above absolute zero, as demonstrated in the preceding sections. These thermally induced vacancies in

pure M—X crystals are called *intrinsic* vacancies. Vacancies may also be induced by impurity ions whose valence differs from the valence of the ions in the host crystal. These are called *extrinsic* vacancies.

Consider the addition of cadmium chloride ($CdCl_2$) to a sodium chloride (NaCl) crystal. From the chemical equations describing the compounds, it is apparent that the valence of the cadmium ion in cadmium chloride is $+2$. The sodium ion in sodium chloride has a valence of $+1$. *One* $CdCl_2$ molecule occupies *two* anion (negative ion) sites, and *one* cation site. Thus, in a dilute solution of cadmium chloride in sodium chloride, there must be one sodium ion vacancy on the M lattice for every cadmium ion added, because electrical neutrality is required (Figure 3.8). This condition of electroneutrality can be expressed as follows:

$$[V'_{Na}] = [Cd^{\cdot}_{Na}] + [V^{\cdot}_{Cl}] \tag{3.58}$$

The concentration of vacancies on the sodium ion lattice is equal to the concentration of vacancies in the chlorine lattice plus the concentration of cadmium ions.

From Eq. 3.58 it is clear that if the concentration of cadmium ions is very much greater than the vacancies of chloride ions ($[Cd^{\cdot}_{Na}] \gg [V^{\cdot}_{Cl}]$), the vacancy in sodium ion concentrations simply equals the concentration of cadmium ions. In this case, the concentration of sodium ion vacancies is *extrinsic*; that is, it is not controlled by the inherent properties of the sodium chloride. It depends on another condition (viz., the cadmium ion concentration) and is not related to the *intrinsic* number of vacancies produced thermally. If, however, the cadmium ion concentration is very small ($[V^{\cdot}_{Cl}] \gg [Cd^{\cdot}_{Na}]$), the concentration of sodium ion vacancies is equal to the concentration of chloride ion vacancies, and the concentrations are intrinsic—that is, only thermally induced.

These relationships can be illustrated using the equilibrium relationship for Schottky defect on the sodium chloride lattice:
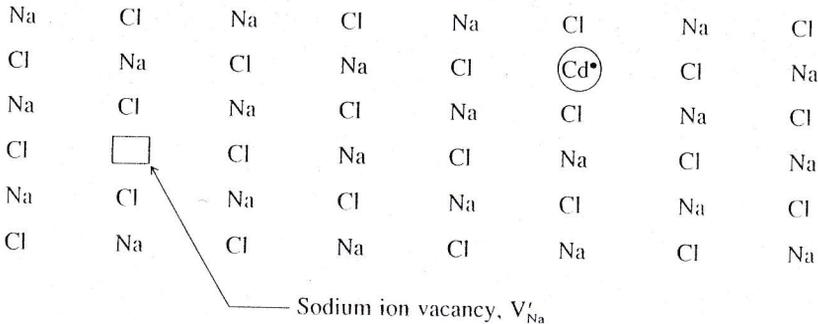
$$K_S = [V'_{Na}][V^{\cdot}_{Cl}] \tag{3.59}$$

Figure 3.8 Effect of $CdCl_2$ addition (presence of $Cd^{\cdot}_{Na}$) on NaCl crystal.

Combining Eqs. 3.59 and 3.58 yields:

$$[V'_{Na}] = [Cd'_{Na}] + \frac{K_S}{[V'_{Na}]}$$

or

$$[V'_{Na}]^2 - [Cd'_{Na}][V'_{Na}] - K_S = 0$$

The solution to this equation is:

$$[V'_{Na}] = \frac{[Cd'_{Na}] + ([Cd'_{Na}]^2 + 4K_S)^{1/2}}{2} \tag{3.60}$$

A sodium chloride crystal with a given concentration of cadmium chloride can display both intrinsic and extrinsic behavior depending on its temperature. This can be understood by considering Eq. 3.60. At higher temperatures, the value of the equilibrium constant K_S can be much greater than the value of $[Cd'_{Na}]^2$. If that is true, then $[V'_{Na}] = K_S^{1/2}$ and the thermally generated imperfections will be greater than the cadmium ion concentration. The crystal will show intrinsic behavior. As the temperature of the crystal drops, the value of K_S drops; that is, the number of thermally induced vacancies drops. When K_S is much smaller than $[Cd'_{Na}]^2$, we will see $[V'_{Na}] = [Cd'_{Na}]$ and extrinsic behavior. This change in behavior with temperature
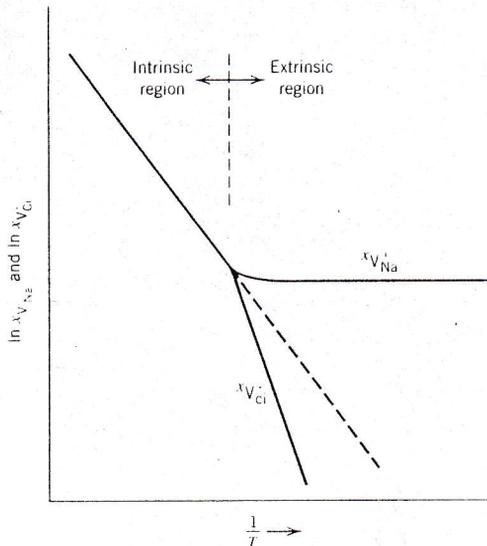

Figure 3.9 Intrinsic and extrinsic vacancy regions.

is illustrated in Figure 3.9, which plots the natural log of a sodium ion vacancy against the inverse absolute temperature.

In the intrinsic region, the vacancies in sodium ions are equal to the vacancies in chloride ions. In the extrinsic region, the equilibrium expression (from Eq. 3.43) must still be observed; thus the vacancies in chloride ions will be less than the quantity calculated for intrinsic chloride ion concentration as illustrated in Figure 3.9.

3.11   EXPERIMENTAL DETERMINATION OF DEFECT TYPE

The different defect types in ionic solids discussed so far should manifest themselves in physically observable ways. In fact, if the ionic solids are to be used as sensors, we want to observe a variation of some measurable quantity as a function of temperature, or of the environment in which the solid exists. This section discusses two ways of inferring defect type in ionic crystals, one based on the measurement of lattice parameters and densities, and the other based on the measurement of electrical conductivity.

As an example of the use of density and lattice parameter measurements, consider the case of the addition of calcia (CaO) to zirconia (ZrO_2). If 15 mol % calcia is incorporated in the zirconia lattice, and assuming that the valences of the ions are unchanged at Ca^{2+}, Zr^{4+}, and O^{2-}, electroneutrality among the three ionic species present yields a composition of $Zr_{0.85}Ca_{0.15}O_{1.85}$. There are two ways of forming this crystal. Either vacancies form on the oxygen lattice, or the calcium and/or zirconium ions enter interstitial positions. It is known from X-ray diffraction studies that the material crystallizes in a fluorite structure with a lattice parameter of 5.131 Å. Let us calculate the expected densities of the crystal for the two cases. If oxygen ion vacancies were to form, the unit cell weight would be $452.60/N_A$, which is the sum of:

$$
\left.
\begin{array}{ll}
\text{Ca:} & \dfrac{0.15 \times 4 \times 40.08}{N_A} \\[2mm]
\text{Zr:} & \dfrac{0.85 \times 4 \times 91.22}{N_A} \\[2mm]
\text{O:} & \dfrac{1.85 \times 4 \times 16}{N_A}
\end{array}
\right\} = \dfrac{452.60}{N_A}
$$

The volume of the unit cell is the cube of the lattice parameter, or 135.08 Å^3, or 135.08×10^{-24} cm^3.
The density would be:

$$
\rho = \frac{452.60}{(6.022 \times 10^{23})(135.08 \times 10^{-24})} = 5.57 \text{ g/cm}^3
$$

If interstitial calcium and zirconium ions formed, then the weight of the unit cell would be $489.29/N_A$ which is the sum of:

$$
\left.
\begin{array}{ll}
\text{O:} & \dfrac{8 \times 16}{N_A} \\[3mm]
\text{Ca:} & \dfrac{4 \times 0.15 \times (2/1.85) \times 40.08}{N_A} \\[3mm]
\text{Zr:} & \dfrac{4 \times 0.85 \times (2/1.85) \times 91.22}{N_A}
\end{array}
\right\} = \dfrac{489.29}{N_A}
$$

The density would be:

$$
\rho = \frac{489.29}{(6.022 \times 10^{23})(135.08 \times 10^{-24})} = 6.01 \ \text{g/cm}^3
$$

The two values 5.57 and 6.01 g/cm³ can be easily distinguished by density measurements. In this case, oxide ion vacancies are found to be present in CaO-ZrO₂ solutions equilibrated at 1600°C.[6] This is an especially important conclusion, because "doped" crystals of zirconia are useful as oxide ion conductors in high temperature fuel cells and as oxygen pressure sensors when used in electrochemical cells (Vol. I, section 6.8).

Electrical conductivity measurements also can be used to determine the types of defect present in ionic crystals. Consider the case of zinc oxide (ZnO). If zinc oxide is heated at low oxygen pressures, it will become conductive. By Hall effect measurements (Refs. 6 and 7), it can be shown that the conducting species is negatively charged, and by the magnitude of the conductivity it is assumed that it is electrons (n') that are the charge carriers. Let us hypothesize that the defect structure is of the Frenkel type, with zinc ions occupying the interstitial position. The question is whether an interstitial zinc ion in the sample is singly or doubly charged. If it is singly charged, then the chemical reaction is:

$$
ZnO = \tfrac{1}{2}O_2 + Zn_i^{\cdot} + n' \tag{3.61}
$$

The equilibrium constant for the reaction is:

$$
K = P_{O_2}^{1/2}[Zn_i^{\cdot}][n'] \tag{3.62}
$$

Noting that the concentration of zinc ions must equal the concentration of electrons,

$$
[Zn_i^{\cdot}] = [n'] \tag{3.63}
$$

---

[6]For samples equilibrated at 1800°C there seems to be some ambiguity in the type of defect present (Ref. 11).

then the concentration of electrons, and the conductivity, will be proportional to the negative one-fourth power of the oxygen pressure, as follows:

$$[n'] = [Zn_i^{\cdot}] = K^{1/2}P_{O_2}^{-1/4} \tag{3.64}$$

If the interstitial zinc ion is doubly charged, concentration of electrons will be proportional to the negative one-sixth power of the oxygen pressure.

$$ZnO = \tfrac{1}{2}O_2 + Zn_i^{\cdot\cdot} + 2n' \tag{3.65}$$

$$[Zn_i^{\cdot\cdot}] = \tfrac{1}{2}[n']$$
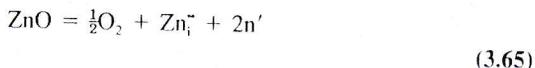
$$[n'] = \tfrac{1}{4}KP_{O_2}^{-1/6} \tag{3.66}$$

The conductivity of zinc oxide crystals is found to be proportional to the negative one-fourth power of the oxygen pressure, hence singly ionized interstitial zinc ions exist in ZnO.

3.12   NON STOICHIOMETRY

Strongly ionic compounds, such as those containing halides, generally display a fixed ratio of constituents. Sodium chloride, for example, shows a one-to-one ratio of cations to anions, cadmium chloride a two-to-one ratio. Many of the compounds studied in elementary chemistry are of this type. We have demonstrated that through exposure to different atmospheres, these ratios may be changed somewhat. In fact, there are compounds in which the ratios vary greatly from the expected stoichiometric ratios. A classic example is provided by one of the iron oxides, wustite.

The compound FeO (wustite) does not exist with a one-to-one cation-to-anion ratio and actually has a range of compositions (Figure 3.10). The iron-rich limit of the compound has a composition closer to $Fe_{0.95}O$. At 1200°C the oxygen content of the wustite may be varied by equilibrating samples in atmospheres with effective oxygen pressures between 10^{-9} and 10^{-12} atm. The departure from stoichiometry may be due either to the formation of oxygen ion interstitials or to cation vacancies. The data in Table 3.3 indicate that the nonstoichiometry is due to cation vacancies because the density of the oxide decreases as the ratio of iron to oxygen decreases. To maintain electroneutrality of the compound, two of the Fe^{2+} ions must be transformed into Fe^{3+} ions for each of the vacancies formed. In chemical terms, this may be considered to be a solution of Fe_2O_3 in FeO. Similar nonstoichiometric behavior is observed in many systems, such as Ni–O, Co–O, and Cu–O. Not all of the nonstoichiometry is accounted for by cation vacancies. In the Zr–O and Ti–O systems, anion vacancies form. As demonstrated in Section 3.10, interstitial cations account for nonstoichiometry in the Zn–O system. Thus we can conclude that the principle
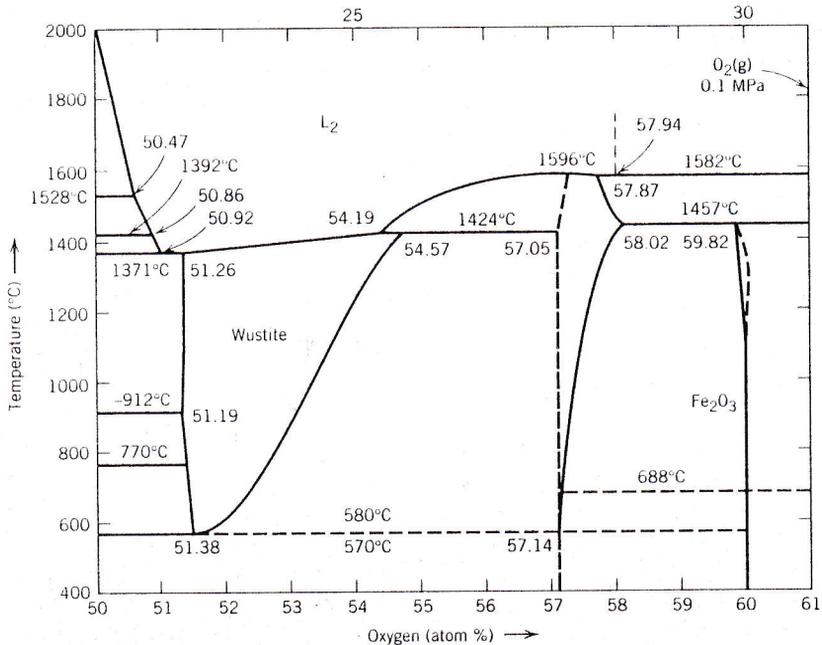
Figure 3.10 Phase diagram for Fe–O from 50 to 60 atom % O; condensed system, 0.1 MPa.

Table 3.3 Lattice Parameter and Density of FeO

Composition	Lattice Parameters	Density (g/cm^3)
$Fe_{0.91}O$	4.282	5.613
$Fe_{0.92}O$	4.285	5.624
$Fe_{0.93}O$	4.292	5.658
$Fe_{0.945}O$	4.301	5.728

Source: E. R. Jette and F. Foote, *J. Chem. Phys.,* 1, 29 (1933), quoted in Ref 12.

of fixed ratios of atoms in molecules that simplified many of the considerations in elementary chemistry does not apply to many solid compounds.

REFERENCES

1. Simmons, R. O., and Balluffi, R. W., *Phys. Rev., 117,* 52 (1960).
2. Simmons, R. O., and Balluffi, R. W., *Phys. Rev., 119,* 600 (1960).
3. Desonbo, W., and Turnbull, D., *Acta Met., 7,* 83 (1959).
4. Bauerle, J. E., and Koehler, J. S., *Phys. Rev., 107,* 1493 (1957).

5. Darken, L. S., *National Physical Laboratory Symposium No. 9*, Paper 4G, Her Majesty's Stationery Office, London, 1959.
6. Solymar, L., and Walsh, D., *Lectures on the Electrical Properties of Materials*, Oxford University Press, New York, 1988.
7. Omar, M. A., *Elementary Solid State Physics*, Addison-Wesley, Reading, MA, 1975.
8. Kroger, F. A., and Vink, V. J., *Solid State Phys.*, 3, 307–435 (1956).
9. Allen, S. M., and Thomas, E. L., class notes for course 313, Massachusetts Institute of Technology, 1994.
10. Brouwer, G., *Philips Res. Rep.*, 9, 366 (1954).
11. Diness, A., and Roy, R., *Solid State Commun.*, 3, 123 (1965).
12. Swalin, Richard A., *Thermodynamics of Solids*, second edition, Wiley, New York, 1972.

PROBLEMS

3.1 When CaO is dissolved in ZrO_2, oxide ion vacancies are created on the zirconia lattice. Calculate the fraction of oxide ion sites that will be vacant when one mole percent of calcium oxide is added to (i.e., dissolved in) the zirconia. Neglect the intrinsic oxide ion vacancies.

What is the oxide ion vacancy concentration stated at vacancies per cubic centimeter? The density of zirconia is about 5.5 g/cm^3.

3.2 Silver bromide (AgBr) exhibits Frenkel imperfections. The formation enthalpy is about 0.60 eV per pair. Assume that the formation entropy is zero.

(a) What fraction of the Ag^+ ions are in interstitial sites just below the melting point of silver bromide?

(b) The Ag^+ ions are extremely mobile, permitting the establishment of equilibrium even at relatively low temperatures. Assume that a one cubic centimeter sample of an AgBr crystal is cooled slowly enough to maintain equilibrium. At what temperature will the crystal contain just one Frenkel pair?

For AgBr:

$$Density = 6.47 \ g/cm^3$$
$$Molecular \ weight = 187.8 \ g/mol$$
$$Melting \ point = 700 \ K.$$

3.3 The formation enthalpy of a Schottky defect in NaCl is about 1.87 eV.

(a) Plot the fraction of Na^+ and Cl^- vacancies as a function of the reciprocal temperature from the melting point, 1074 K, to 300 K. Assume that the formation entropy of the vacancies is zero.

(b) Repeat part a, assuming that 10^{-6} mole fraction of $CaCl_2$ is added to the pure NaCl. Why are the plots in parts a and b different?

3.4 Density measurements are often used to determine the type of defects created when impurities are dissolved in ionic crystals. If one assumes that the dissolution of aluminum oxide (Al_2O_3) in pure magnesium oxide (MgO) creates vacancies on the positive ion lattice, calculate the fractional change in the density of pure MgO when one weight percent of Al_2O_3 is added to it.

Assume that the crystal structure and the lattice parameter of MgO do not change with the addition of the alumina.

3.5 The energy of formation for vacancies in gold is about 0.9 eV. Assuming that there is no change in vibrational entropy associated with the formation of a vacancy, calculate the intrinsic vacancy concentration in gold at 500 and 1000 K.

Silver, when dissolved in gold, exhibits a binding energy of about 0.10 eV with vacancies. Calculate the total vacancy concentration in gold at 500 and 1000 K. Assume that there is no change in vibrational entropy involved in the formation of the silver–vacancy complex. The silver concentration is 0.1 mol percent.

The density of gold is about 19.3 g/cm^3.

3.6 Magnesium oxide (MgO) is known to form Schottky defects, creating vacancies on both the cation (Mg) and anion (O) lattices. The energy of formation of a Schottky defect in MgO is estimated to be about 6 eV. Assume that we can consider the entropy of formation of the defect to be zero [the preexponential term, $\exp(\Delta S/2R) = 1$].

(a) Estimate the fraction of Mg sites and O sites vacant at equilibrium at 1800 K.

(b) What is the concentration of Mg vacancies (vacancies per cubic centimeter) at equilibrium at 1800 K?

(c) If a sample of MgO with 0.1 mol % of zirconia (ZrO$_2$) is prepared, what will be the fraction of Mg sites unoccupied at equilibrium at 1800 K? What will be the fraction of oxygen sites unoccupied? The substitution of zirconium ions (Zr^{+4}) in the lattice results in cation vacancies.

DATA

Density of MgO = about 3.58 g/cm^3
Atomic weight of Mg = 24.3 g/mol
Atomic weight of oxygen = 16 g/mol

3.7 A sample of iron oxide (wustite) has a composition Fe$_{0.93}$O. Its lattice parameter is found to be 4.301 Å.

(a) Calculate the density of the sample (g/cm^3), assuming that the nonstoichiometry of the compound is accounted for by vacancies on the Fe lattice.

(b) Calculate the density of the sample (g/cm^3), assuming that the nonstoichiometry of the compound is accounted for by oxygen interstitials.

DATA

Atomic weights
Fe = 55.85 g/mol
O = 16 g/mol

FeO has a "rock salt" crystal structure (fcc) with 4 cations and 4 anions per unit cell in a perfect (defect-free) crystal.

3.8 Given the information below, you are asked to estimate the number of neutral (noncharged) vacancies in pure, metallic silicon at 1200 K.

(a) What fraction of the silicon sites are vacant at 1200 K (at equilibrium)?
(b) What is the concentration of these vacancies (per cubic centimeter)?

DATA

ΔH_f = 2.4 eV per vacancy
$\exp(+\Delta S_f/k)$ = 3.0 for the vacancy
Atomic weight of silicon = 28 g/cm³
Density of silicon = 2.42 g/cm³

3.9 The accompanying graph shows the self-diffusion coefficient for Na^+ in an NaCl crystal doped with $CdCl_2$. NaCl is believed to form Schottky defects. Using the data in the graph, calculate the following.

(a) The activation energy for self-diffusion of Na^+ in NaCl.
(b) The enthalpy of formation of Schottky defects in NaCl (in eV).