

Chapter 2

Defects In Ceramics

To this point we have primarily discussed the ideal crystalline state. However, a great many properties of crystals are determined by imperfections. Electrical conductivity and diffusional transport (the topic of the following chapter) in most ceramics is determined by the number and type of point defects. Various optical properties, for instance those giving rise to color and lasing activity, are caused by electronic absorption and emission processes at impurity ions and other point defects. The rates of kinetic processes such as precipitation, densification, grain coarsening, and high-temperature creep deformation are determined by mass transport due to defects.

We will confine most of our discussion to *point defects*,¹ defined as deviations from the perfect atomic arrangement: missing ions, substituted ions, interstitial ions, and their associated valence electrons. Point defects occur (to greater or lesser degrees) in all crystalline materials. A principle difference between point defects in ionic solids and those in metals is that in the former, all such defects can be electrically charged. *Ionic defects* are point defects that occupy lattice atomic positions, including vacancies, interstitials, and substitutional solutes. *Electronic defects* are deviations from the ground state electron orbital configuration of a crystal, formed when valence electrons (i.e., those responsible for bonding) are excited into higher orbital energy levels. Such an excitation may create an electron in the conduction band and/or an electron hole in the valence band of the

¹ Point defects may be distinguished from *extended defects*, which also play an important role in determining crystal and polycrystal properties. These include aggregates of point defects in *clusters*, *line defects* such as dislocations, which have their most important role in plastic deformation, as well as various *planar defects*. Planar defects include external surfaces, grain boundaries, stacking faults, and crystallographic shear planes.

hand, a variety of foreign atoms can substitute in the octahedral sites for the host cations, as long as charge neutrality can be maintained. A corollary is that crystal structures that are not close-packed, such as silicon nitride (Fig. 1.38) or the various crystalline forms of silicon dioxide (Figs. 1.39, 1.40) often readily accommodate interstitial atoms. The extensive solid solutions known as silons and β -quartz solid solutions (see also the discussion of glass ceramics in Chapter 5) form in these two respective structures due to the availability of interstitial sites for charge-compensating cations.

Some caution is necessary in applying this simple line of reasoning, since unoccupied interstitial sites in close-packed ionic structures are empty for good reason: The atomic arrangement minimizes repulsive electrostatic interaction with second-nearest neighbors of the same kind. For example, corundum (Al_2O_3) has only two-thirds of the octahedral sites filled, yet theoretical calculations and experiments both indicate that the energy to displace an aluminum ion to an interstitial site (Frenkel energy) is higher than the formation energies of other defects. The same is true in rutile, where only one-half of the octahedral cation sites are filled.

The location of solutes and impurities in the lattice often depends on the compatibility in size and valence with host ions. Solute that differ in valence from the host ion (known as *aliovalent* solutes) must be compensated by additional charged defects in order to maintain overall electrical neutrality in the crystal. An important part of the total energy for solute incorporation is the energy to form the charge-compensating defects, and it can be misleading to consider only the energetics for substituting the solute ion.

Chemical composition will often suggest the presence of certain defects. *Nonstoichiometric* compounds are those in which the metal/anion ratio deviates significantly from the ideal value on which the structure is based, due to the existence of multiple ion valence states. Transition metal oxides (e.g., NiO , FeO , Fe_3O_4 and TiO_2) are often highly defective. For example, wüstite (Fe_{1-x}O), which crystallizes in the rocksalt structure type, is cation-deficient due to the presence of a significant fraction (at least 5%) of the iron being in the Fe^{3+} state. One can deduce that there must be either cation vacancies or oxygen interstitials present to accommodate the deviation from a perfect 1:1 stoichiometry. Knowing that the rocksalt structure is based on close-packing of the (larger) anions, it is reasonable to suppose that cation vacancies are more easily formed than are oxygen interstitials. Another type of compositional deviation, which suggests a high defect concentration, is an extensive solid solution with an aliovalent solute. One example is the solid solution of CaO in ZrO_2 , where a concentration of oxygen vacancies equal to the calcium concentration is formed.

Electrical conductivity is directly related to the concentration of mobile electronic defects, and a crystal that is observed to be electrically very insulating can be assumed to have negligible concentrations of free electrons and electron holes. Conversely, in semiconducting or metallically conducting ceramics, the concentrations of electrons or holes are comparatively plentiful and are the defects of

crystal. In terms of spatial positioning, these defects may be localized near atom sites, in which case they represent changes in the ionization state of an atom, or may be delocalized and move freely through the crystal. Point defects in ceramic systems can be formed by thermal excitation at high temperature, by the addition of solutes and impurities, or by oxidation or reduction processes which cause a variation in the metal/anion stoichiometry of the compound.

Isolated charged defects in crystals are also able to interact with one another in an analogous way to the interactions which take place between different ions or between ions and electrons in aqueous solutions. In the solid-state analogy, the perfect crystal may be regarded as a neutral medium into which the charged defects are dissolved. This fruitful similarity between solution-chemical interactions and solid-state defect interactions has resulted in the development of the field known as *defect chemistry*, which provides immensely useful tools for understanding the properties of crystals containing point defects.

2.1 POINT DEFECTS

In considering point defect behavior, one is usually concerned with two principal issues: what types of point defects are present, and in what concentration? The answer depends greatly on crystal structure, chemical composition, and bonding, as well as the temperature of interest. Physical properties such as density, melting point, electrical conductivity, diffusion, and optical absorption often provide strong clues to defect behavior. The formation of atomic defects requires the breaking of interatomic bonds, and in the same way that the melting (or decomposition) temperature of a compound scales with the strength of its interatomic bonding, so does the energy to create atomic defects. Within compounds of a given structure type (e.g., rocksalt structure type alkali halides and oxides), the energy to form defects scales with the melting point. Due to the importance of melting temperature as a parameter, defect and diffusional properties are sometimes scaled to the *homologous temperature*, T/T_m , when comparing different materials. At equal temperature, the concentration of defects in MgO ($T_m = 2825^\circ\text{C}$) is many orders of magnitude lower than that in the alkali halides (NaCl , KCl , LiF , etc.), which have melting points below 1000°C . (Many earlier studies of point defects were conducted in alkali halides due to their simple structures and a relative abundance of defects.) At equal homologous temperature, however, the defect concentrations are rather similar.

Another simple consideration is the availability of defect sites in the crystal structure. A close-packed sublattice of ions does not easily accommodate interstitial defects. For instance, in the rocksalt structure, anion interstitials have a high energy relative to other defects such as anion vacancies, cation vacancies and cation interstitials. Furthermore, since all octahedral sites in the cation sublattice are filled, only the smaller tetrahedral sites are possible interstitial atom locations. Thus in this structure one finds that interstitial defects are unlikely to form unless the atom in question is quite small (such as H or Li). On the other

primary interest. Note that unlike atomic defects, the intrinsic concentration of these charge carriers does *not* scale with the melting point. Instead, the *type* of bonding is much more important, since the extent to which electrons are shared among the orbitals of adjacent atoms determines the ease with which they can be excited. As a rule, highly ionic ceramics have larger bandgaps than do covalent ceramics, and lower intrinsic carrier concentrations. For instance, pure NaCl has a bandgap of 7.3 eV and is much more electrically resistive than pure SiC, which has a bandgap of 2.9 eV, even though the latter is much more refractory and does not decompose until 3000°C. The electrical conductivity of compounds also depends greatly on the concentration of impurities. Furthermore, electrical conductivity in ceramics can also result from ion motion, so that the observation of high conductivity alone is not sufficient to conclude that the concentration of electrons or holes is significant. This is discussed further in Chapter 3. The diffusion rate of atoms is also strongly dependent on defect concentrations, and if the rate of a diffusion-controlled process such as phase separation or sintering or creep deformation is particularly slow or fast, it may suggest that particular ionic defects are negligible or abundant.

From these and other clues, it is often possible to make a reasonable guess as to the dominant defects in a particular material. Since it is difficult to directly observe atomic defects, verification is usually based on correlations between expected changes in physical properties and experimental data. Examples are given later in this chapter and in Chapter 3. Computer simulation methods have also proven useful in evaluating the relative stability of different defect types. While a detailed discussion of these techniques is beyond the scope of our discussion, the basic approach is to calculate the lattice energy of a crystal with and without defects, the difference between which is then the formation energy of the defect.

Intrinsic Ionic Disorder

Starting with a perfect crystal, one can only form atomic defects with an expenditure of energy, which is most commonly thermal, although radiation of various kinds can also displace atoms. The increased energy and amplitude of lattice vibrations at elevated temperatures increase the probability that an atom will be displaced from its lattice position. Thus the formation of atomic defects is a *thermally activated* process, in which the defect formation energy represents the activation barrier. In many ceramic systems, significant concentrations of defects are formed only at temperatures well above half the melting point.

One may ask, if a positive energy expenditure is necessary to form defects in the first place, what allows there to be a finite concentration of defects? We will show that the increase in energy upon forming the defects is counterbalanced by the decrease in free energy which results from an increase in the entropy of the system. This additional entropy is mostly configurational, resulting from the distribution of a small number of defects over a large number of lattice sites. Thus point defects in solids are *entropically stabilized*.

The two most common types of crystalline defects in ionic materials are *Frenkel* and *Schottky* defects. We term these *intrinsic* defects since they can be thermally generated in a perfect crystal, as opposed to *extrinsic* defects, which are formed only by the addition of impurities or solutes. A Frenkel defect (Fig. 2.1) is formed when an atom is displaced from its normal site onto an interstitial site forming a defect pair: a vacancy and an interstitial. In ionic materials, both the cation and the anion can undergo this kind of displacement (the anion Frenkel is sometimes referred to as an anti-Frenkel). In metals and covalent compounds Frenkel defects can also form; they differ from those in ionic compounds only in that the defects need not be electrically charged.

The Schottky defect is unique to ionic compounds and is represented by the simultaneous creation of both cation and anion vacancies, which is illustrated in Fig. 2.2. The vacancies must be formed in the stoichiometric ratio in order to preserve the electrical neutrality of the crystal. Thus in NaCl and MgO, one forms a Schottky *pair*, while in TiO₂ the Schottky defect consists of three defects (one titanium vacancy and two oxygen vacancies), and in Al₂O₃, the Schottky defect is a quintuplet (two aluminum vacancies, three oxygen vacancies). The total number of lattice sites is increased by one formula unit upon formation of a Schottky defect, unlike the Frenkel defect, which conserves the number of lattice sites.

Concentration of Intrinsic Defects. In order to understand the factors that determine the concentration of intrinsic defects, let us consider the change in free energy of a perfect crystal with initial free energy G_0 upon forming n Frenkel defect pairs at an energy expense of Δg_f per pair. The free energy of the crystal becomes:

$$G = G_0 + n\Delta g_f - T\Delta S_c \quad (2.1)$$

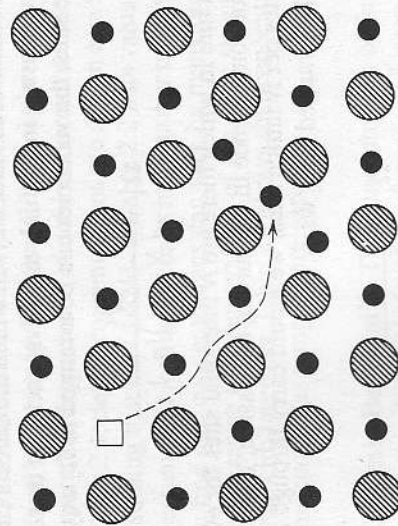


Fig. 2.1 Frenkel disorder. Ion leaving normal site forms an interstitial ion and leaves a vacancy.

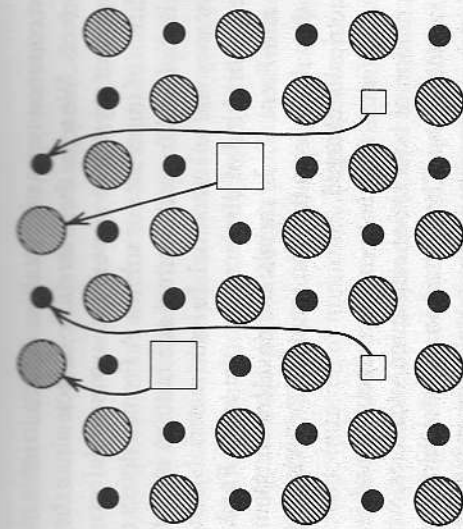


Fig. 2.2 Schottky disorder. Displacement of anion and cation to surface leaves a pair of vacancies.

where ΔS_c is the increase in configurational entropy of the crystal. The change in free energy is therefore:

$$\Delta G = (G - G_0) = n\Delta g_f - T\Delta S_c \quad (2.2)$$

The magnitude of both of the terms on the right-hand side is dependent on the number of defects n . The *equilibrium* number of defects is found by minimizing ΔG with respect to n . To determine this equilibrium concentration, we must first evaluate the configurational entropy ΔS_c , which is given by:

$$\Delta S_c = k \ln \Omega \quad (2.3)$$

where Ω is the number of distinct ways in which the defects can be arranged. For n Frenkel pairs we have n_i interstitials and n_v vacancies. If these are arranged on a total of N lattice sites, the vacancies can be arranged in Ω_v ways, where:

$$\Omega_v = \frac{N!}{(N - n_v)!n_v!} \quad (2.4)$$

assuming a structure in which there are N interstitial sites for every N lattice sites (this is simply for convenience in the current discussion; if for instance there are $2N$ interstitial sites per N lattice sites, we would carry through a factor of 2). The interstitials can be arranged in Ω_i ways:

$$\Omega_i = \frac{N!}{(N - n_i)!n_i!} \quad (2.5)$$

The total number of configurations is then $\Omega = \Omega_i \Omega_v$. Since we've formed the defects in pairs, $n_i = n_v = n$. The configurational entropy is therefore given by:

$$\Delta S_c = k \ln \left(\frac{N!}{(N - n_v)!n_v!} \right) \left(\frac{N!}{(N - n_i)!n_i!} \right) = 2k \ln \left(\frac{N!}{(N - n)!n!} \right) \quad (2.6)$$

For large numbers N and n (e.g., a mole of atoms) Stirling's approximation can be used: $\ln N! = N \ln N - N$. The configurational entropy is then:

$$\Delta S_c = 2k \left[N \ln N - (N - n) \ln(N - n) - n \ln n \right] \quad (2.7)$$

and the total free energy change is

$$\Delta G = n\Delta g - 2kT \left[N \ln \left(\frac{N}{N - n} \right) + n \ln \left(\frac{N - n}{n} \right) \right] \quad (2.8)$$

To find the equilibrium concentration of defects, we evaluate the derivative $(\partial \Delta G / \partial n)_{T,P} = 0$, keeping in mind that for dilute concentrations of defects, $(N - n) \sim N$. After rearrangement we obtain the following result for the concentration of defects (given as the fraction of the total number of atoms N):

$$\frac{n}{N} = \exp \left(-\frac{\Delta g}{2kT} \right) = \exp \left(\frac{\Delta s}{2k} \right) \exp \left(-\frac{\Delta h}{2kT} \right) \quad (2.9)$$

A most important result given by Eq. 2.9 is that the defect concentration of defects is exponentially dependent on the formation free energy, Δg , and on temperature. Note that the entropy Δs is not the configurational entropy, which we have already accounted for (ΔS_c), but is the nonconfigurational entropy associated with lattice strains and changes in vibrational frequencies accompanying the defect. It is sometimes assumed that Δs is much less than the configurational entropy, such that $\exp(\Delta s/2k) \sim 1$. However, this assumption can be seriously in error, as values of $\exp(\Delta s/2k)$ ranging from 10^{-4} to 10^4 have been deduced from experimental data. As a result, the absolute concentrations of intrinsic defects can be difficult to determine to a high level of accuracy. Relative differences between different compounds, and the temperature dependence of defect concentrations, are more easily determined. In Table 2.1, defect concentrations are shown as a function of Δh and temperature, assuming that $\exp(\Delta s/2k) \sim 1$. Table 2.2 lists values of Δh for the most prevalent (lowest-energy) intrinsic defects in a number of systems. Comparing these values, we find that concentrations can vary by many orders of magnitude at a constant temperature between systems of the same structure type (e.g., rocksalt). For systems with large Δh , Table 2.1 shows that concentrations change by many orders of magnitude as temperature varies.

Intrinsic versus Extrinsic Behavior. The concentration of intrinsic defects can be exceedingly small in highly refractory ceramics of large defect formation energy. As a result, solutes and especially aliovalent solutes which are accompanied by the formation of extrinsic vacancies or interstitials have a great importance in determining overall defect behavior. Oxidation and reduction pro-

Table 2.1 Defect Concentration at Different Temperatures

$$\frac{n}{N} = \exp\left[-\frac{\Delta g}{2kT}\right] = \exp\left[\frac{\Delta s}{2k}\right] \exp\left[-\frac{\Delta h}{2kT}\right] \approx \exp\left(-\frac{\Delta h}{2kT}\right)$$

Defect Concentration	1eV ^a	2eV	4eV	6eV	8eV
<i>n</i> / <i>N</i> at 100°C	2 × 10 ⁻⁷	3 × 10 ⁻¹⁴	1 × 10 ⁻²⁷	3 × 10 ⁻⁴¹	1 × 10 ⁻⁵⁴
<i>n</i> / <i>N</i> at 500°C	6 × 10 ⁻⁴	3 × 10 ⁻⁷	1 × 10 ⁻¹³	3 × 10 ⁻²⁰	8 × 10 ⁻²⁷
<i>n</i> / <i>N</i> at 800°C	4 × 10 ⁻³	2 × 10 ⁻⁵	4 × 10 ⁻¹⁰	8 × 10 ⁻¹⁵	2 × 10 ⁻¹⁹
<i>n</i> / <i>N</i> at 1000°C	1 × 10 ⁻²	1 × 10 ⁻⁴	1 × 10 ⁻⁸	1 × 10 ⁻¹²	1 × 10 ⁻¹⁶
<i>n</i> / <i>N</i> at 1200°C	2 × 10 ⁻²	4 × 10 ⁻⁴	1 × 10 ⁻⁷	5 × 10 ⁻¹¹	2 × 10 ⁻¹⁹
<i>n</i> / <i>N</i> at 1500°C	4 × 10 ⁻²	1 × 10 ⁻⁴	2 × 10 ⁻⁶	3 × 10 ⁻⁹	4 × 10 ⁻¹²
<i>n</i> / <i>N</i> at 1800°C	6 × 10 ⁻²	4 × 10 ⁻³	1 × 10 ⁻⁵	5 × 10 ⁻⁸	2 × 10 ⁻¹⁰
<i>n</i> / <i>N</i> at 2000°C	8 × 10 ⁻²	6 × 10 ⁻³	4 × 10 ⁻⁵	2 × 10 ⁻⁷	1 × 10 ⁻⁹

^a1eV = 23.05 kcal/mole.

cesses also cause point defects to be introduced, the concentrations of which can exceed that of the intrinsic ionic defects.² Whether a defect structure is considered "intrinsic" or "extrinsic" is solely based on the relative concentrations. Intrinsic defect concentrations increase with temperature, as discussed above. Extrinsic defects, with the exception of nonstoichiometry, remain largely constant in concentration. Thus at higher temperatures, the likelihood of intrinsic behavior increases. However, in some materials the formation energies of intrinsic defects are so high, and the resulting concentrations so low, that intrinsic behavior is virtually never encountered.

As an example, let us consider the relative importance of intrinsic defects in two compounds of rocksalt structure type, NaCl and MgO. In both, the dominant intrinsic defect is the Schottky defect, as opposed to cation or anion Frenkel defects. For charge neutrality, the concentrations of cation and anion vacancies must be equal. From Eq. 2.9 we can write the concentration of each vacancy as

$$n_i/N \sim \exp[-\Delta h_i/2kT]$$

Table 2.2 shows that the Schottky formation enthalpy for MgO (~7.7 eV) is much higher than that for NaCl (~2.4 eV), consistent with the stronger bonding and higher melting temperature (2825°C vs. 801°C) of the former. At 700°C, MgO clearly has many orders of magnitude fewer intrinsic Schottky defects. Scaled to the homologous temperature, the concentrations are not so different; at its melting point NaCl has a defect concentration of $\sim 2 \times 10^{-6}$ (2 parts per million, ppm) and MgO has $\sim 4 \times 10^{-7}$ (0.4 ppm).

² There is not a consistent formalism that regards defects due to oxidation and reduction, i.e., nonstoichiometry, as either intrinsic or extrinsic. This is primarily a matter of semantics, and for the purposes of this discussion we will consider them to be extrinsic.

Table 2.2 Some Defect Energies of Formation

Compound	Reaction	Energy of Formation Δh (eV)
AgCl	$\text{Ag}_{\text{Ag}}^x \Leftrightarrow \text{Ag}_i + V'_{\text{Ag}}$	1.1
NaCl	$\text{null} \Leftrightarrow V'_{\text{Na}} + V_{\text{Cl}}$	2.2–2.4
KCl	$\text{null} \Leftrightarrow V'_{\text{K}} + V_{\text{Cl}}$	2.6
LiF	$\text{null} \Leftrightarrow V'_{\text{Li}} + V_{\text{F}}$	2.4–2.7
CsCl	$\text{null} \Leftrightarrow V'_{\text{Cs}} + V_{\text{Cl}}$	1.86
BeO	$\text{null} \Leftrightarrow V''_{\text{Be}} + V_{\text{O}}$	~6
MgO	$\text{null} \Leftrightarrow V''_{\text{Mg}} + V_{\text{O}}$	7.7
CaO	$\text{null} \Leftrightarrow V''_{\text{Ca}} + V_{\text{O}}$	~6
BaO	$\text{null} \Leftrightarrow V''_{\text{Ba}} + V_{\text{O}}$	3.4
MnO	$\text{null} \Leftrightarrow V''_{\text{Mn}} + V_{\text{O}}$	4.6
FeO	$\text{null} \Leftrightarrow V''_{\text{Fe}} + V_{\text{O}}$	6.5
ZnO	$\text{O}_{\text{O}}^x \Leftrightarrow \text{O}''_i + V_{\text{O}}$	2.51
Li ₂ O	$\text{Li}_{\text{Li}}^x \Leftrightarrow \text{Li}_i + V'_{\text{Li}}$	2.28
CaF ₂	$\text{F}_{\text{F}}^x \Leftrightarrow V_{\text{F}} + F'_i$	2.3–2.8
	$\text{Ca}_{\text{Ca}}^x \Leftrightarrow V''_{\text{Ca}} + \text{Ca}_i$	~7
	$\text{null} \Leftrightarrow V''_{\text{Ca}} + 2V_{\text{F}}$	~5.5
UO ₂	$\text{O}_{\text{O}}^x \Leftrightarrow \text{O}''_i + V_{\text{O}}$	5.1
	$\text{U}_{\text{U}}^x \Leftrightarrow V''''_{\text{U}} + \text{U}_i$	~9.5
	$\text{null} \Leftrightarrow V''''_{\text{U}} + 2V_{\text{O}}$	~6.4
TiO ₂ (rutile)	$\text{null} \Leftrightarrow V''''_{\text{Ti}} + 2V_{\text{O}}$	5.2
	$\text{O}_{\text{O}}^x \Leftrightarrow \text{O}''_i + V_{\text{O}}$	8.7
	$\text{Ti}_{\text{Ti}}^x \Leftrightarrow \text{Ti}_i + V''''_{\text{Ti}}$	12
α -Al ₂ O ₃	$\text{null} \Leftrightarrow 2V''_{\text{Al}} + 3V_{\text{O}}$	20.1–25.7 (4.2–5.1 eV/defect)
	$\text{Al}_{\text{Al}}^x \Leftrightarrow \text{Al}_i + V''_{\text{Al}}$	10.4–14.2 (5.2–7.1 eV/defect)
	$\text{O}_{\text{O}}^x \Leftrightarrow \text{O}''_i + V_{\text{O}}$	7.6–14.5 (3.8–8.3 eV/defect)
MgAl ₂ O ₄	$\text{null} \Leftrightarrow V''_{\text{Mg}} + 2V''_{\text{Al}} + 4V_{\text{O}}$	29.1 (4.15 eV/defect)

However, there is a great difference in the purity levels attainable in these two materials. With zone-refining procedures, NaCl can be purified to levels below one part-per-million. In contrast, the highest purity MgO currently available has about 50 ppm impurities (because of the much higher processing temperatures necessary, contamination from crucibles and the like is harder to avoid). These impurities are often aliovalent cations. Thus the concentration of "extrinsic" de-

fects, that is, the impurity concentration, is much greater than the intrinsic defect concentration in MgO. As a result, "intrinsic" NaCl can in practice be achieved rather easily, whereas all presently available MgO is likely to be extrinsic at all temperatures up to the melting point.

Units for Defect Concentration. A variety of units are used in the description of defect concentrations, and it is useful to know how to translate between them. The two most common systems of units are the number fraction relative to a particular atom, and the number of defects per unit volume. The concentration n/N discussed above represents the number fraction of defects n relative to the number of possible sites N . This fraction could be expressed in concentration units of atomic fraction (in an elemental solid), cation fraction, or mole fraction. For a compound of 1:1 stoichiometry, the cation fraction, anion fraction, and mole fraction are all equivalent; for other stoichiometries the translation is a simple numerical factor. Frequently the number fractions are expressed as part-per-million (ppm) units, where a fraction of 10^{-6} is 1 ppm. Note that trace chemical analyses are often reported in units of *weight* ppm or weight percent instead.

Defect concentration units of number per unit volume (e.g., no./cm^3 or cm^{-3}) are also commonly used, especially in the discussion of electrical properties. The density of atoms in solids is $\sim 10^{23} \text{ cm}^{-3}$, so a 1 ppm concentration is $\sim 10^{17} \text{ cm}^{-3}$. An exact conversion from mole fraction to number per unit volume requires knowing the molecular weight (MW) and density (ρ) of the compound in question; the number of formula units per unit volume is

$$\frac{N_a (\text{no./mole}) \cdot \rho (\text{g/cm}^3)}{MW (\text{g/mole})}$$

where N_a is Avogadro's number ($6.02 \times 10^{23} \text{ mole}^{-1}$). In this and the following chapter, we will use units of both mole fraction and no./cm^3 , whichever is the more convenient, reflecting common usage in the published literature.

SPECIAL TOPIC 2.1

KRÖGER-VINK NOTATION

A standard notation used for the description of defects in ionic materials is Kröger-Vink notation, in which a defect is described by three parts. The main body of the notation identifies whether the defect is a vacancy "V" or an ion such as "Mg." The *subscript* denotes the site that the defect occupies, either the normal atom sites of the host lattice or an interstitial site "i." The *superscript* identifies the *effective charge* (or *relative charge*) of the defect relative to the perfect crystal lattice. For this part of the notation, dots (·) represent positive effective charges, dashes (′) represent negative charge, and x 's are sometimes used to show neutrality. Let's illustrate with some examples:

$V_{\text{Mg}}^{\cdot\cdot}$ is a vacant magnesium site; V stands for vacancy, the subscript Mg shows that it occupies what is normally a magnesium site, and, the superscript "·" shows that the vacancy has a doubly negative charge relative to the perfect lattice, as there is the *absence* of an Mg^{2+} ion.

$\text{Al}_i^{\cdot\cdot\cdot}$ is an interstitial aluminum ion. The subscript i denotes that the aluminum is interstitial, and the superscript "·" shows that the normally unoccupied interstitial site now has an excess +3 charge due to the Al^{3+} ion.

Some atoms can accept more than one valence state. This is especially common for the transition metal ions. It is therefore possible to have several distinctly different defects for a particular element on a given site with different "ionization" or "oxidation" states. Iron substituted for Mg^{2+} in MgO can be Fe_{Mg}^x (an Fe^{2+} ion) or $\text{Fe}_{\text{Mg}}^{\cdot}$ (if it is Fe^{3+}). In FeO, where the iron oxidation state is predominantly 2+, trivalent iron can also be described as a positive defect, $\text{Fe}_{\text{Fe}}^{\cdot}$.

Clustered defects or *defect associates* are denoted with parentheses that group together the defects that are bound to one another by electrostatic attraction. The net effective charge of the associate is shown with superscripts. For instance, $(V_{\text{Na}}' - V_{\text{Cl}}^{\cdot})^x$ is a clustered pair consisting of one sodium vacancy and one chlorine vacancy, which together are electrically neutral. $(\text{Al}_{\text{Mg}} - V_{\text{Mg}}^{\cdot})^{\cdot}$ is a substitutional aluminum solute (in MgO) bound to a magnesium vacancy. This type of defect is sometimes called a "dimer." The associate $(\text{Al}_{\text{Mg}}^{\cdot} - V_{\text{Mg}}^{\cdot\cdot} - \text{Al}_{\text{Mg}}^{\cdot})^x$ or "trimer" is a cluster of three defects. This notation generally pertains to defects that occupy neighboring sites, since defects of further separation are not as strongly bound.

The *concentration* of defects is denoted by square brackets, for example $[V_{\text{Mg}}^{\cdot\cdot}]$, $[\text{Al}_{\text{Mg}}^{\cdot}]$ and $[(V_{\text{Na}}' - V_{\text{Cl}}^{\cdot})^x]$. A shorthand often used for the concentration of electrons and holes, $[e^{\cdot}]$ and $[h^{\cdot}]$, is n and p , respectively.

Finally, in Kröger-Vink notation we always define defects relative to a "perfect" crystal. For complex ceramics with multiple cations distributed over more than one type of site, such as the spinels (which can have a normal, inverse, or random cation distribution, see Chapter 1), the choice of this reference state can be somewhat arbitrary. Nonetheless, defect chemical notation and the principles discussed herein can be applied as long as the reference system is self-consistent throughout.

Defect Chemical Reactions

We showed previously from a statistical thermodynamic viewpoint how defect concentrations depend on their formation energies and temperature. An equivalent way to view the formation of defects is as a chemical reaction, for which there

is an equilibrium constant which is governed by the law of mass action. For example, the Schottky reactions for NaCl and MgO, respectively, can be written using Kröger-Vink notation as:



and



where null (sometimes "nil") indicates the creation of defects from a perfect lattice. The respective mass-action equilibrium constants are:

$$K_s = [V'_{\text{Na}}][V_{\text{Cl}}] \quad (2.12)$$

and

$$K_s = [V'_{\text{Mg}}][V_{\text{O}}] \quad (2.13)$$

The brackets denote concentration, usually given in mole fraction (equivalent to n_i/N). Writing the equilibrium constant as the product of concentrations implies that the thermodynamic activity of each defect D is equal to its concentration, $a_D = [D]$.³ The free energy for each of these "quasi-chemical" reactions is simply the Schottky formation energy, and the equilibrium constant is given by:

$$K_s = \exp\left(-\frac{\Delta g_s}{kT}\right) \quad (2.14)$$

Notice that the equilibrium constant is a function of temperature only. This dictates that the product of the cation and anion vacancy concentrations (Eqs. 2.12 and 2.13) is a constant at fixed temperature. Furthermore, when only the intrinsic defects are present, the concentration of anion and cation vacancies must be equal for charge neutrality, and so we obtain

$$[V'_{\text{Na}}] = [V_{\text{Cl}}] = \exp\left(-\frac{\Delta g_s}{2kT}\right) \quad (2.15)$$

which is the same result as in Eq. 2.9.

Defect chemical reactions such as Eqs. 2.10 and 2.11 are written for the formation of defects within a solid and must obey *mass*, *site*, and *charge* balance. In this

³ This assumption, namely that we have an ideal solution, is usually good for dilute solutions (<<1%) and sometimes applies for surprisingly concentrated solutions as well. It fails when interactions between defects become significant. When this is the case, activities should be used in place of concentrations. This has the effect of introducing activity coefficients γ into the equilibrium constants. For instance, Eq. 2.13 becomes $K_s = \gamma_{V'_{\text{Mg}}} \gamma_{V_{\text{O}}} [V'_{\text{Mg}}][V_{\text{O}}]$. One method of evaluating these activity coefficients is to use the *Debye-Hückel* theory of electrolytes, discussed briefly in 2.3 and also in references listed at the end of the chapter.

respect they differ somewhat from ordinary chemical reactions, which must obey only mass and charge balance. (Defect chemical reactions are sometimes referred to as *quasi-chemical* reactions.) Mass balance simply means that a chemical reaction cannot create or lose mass. In defect chemistry, we may also write balanced reactions involving defects without mass, as in the Schottky reactions of Eqs. 2.10 and 2.11. Site balance means that the *ratio* of cation to anion sites of the crystal must be preserved, although the total number of sites can be increased or decreased. For instance, in Eqs. 2.10 and 2.11, vacancies are formed in the stoichiometric ratios. And, in order to ensure charge balance under the Kröger-Vink notation system we verify that the total *effective charge* is balanced.

As examples of site balance, consider the Schottky reactions for Al_2O_3 and BaTiO_3 . Cation and anion vacancies must be formed in the stoichiometric ratios, and if so, we find that the effective charges are automatically balanced:



The Frenkel reaction (Fig. 2.9), written in Kröger-Vink notation for the system AgCl (in which this intrinsic mechanism is dominant) is



Site balance is maintained here since the formation of interstitials does not create new crystal sites, but rather occupies pre-existing ones. Mass and charge are also automatically balanced.

We may write all processes involving defect formation or reaction in a crystal as defect chemical reactions. And, as long as mass, site, and charge balance are obeyed, the reaction is formally "correct," no matter how improbable or high in formation energy. Like liquid and gas-phase chemical equilibria, many conceivable defect chemical reactions can simultaneously take place in a solid, even though the relative rates of reaction may differ by many orders of magnitude. It is the most probable reactions that are of greatest interest, and of which there are fortunately only a few that usually need to be considered. In addition to the formation of intrinsic defects, reactions of particular interest include the incorporation of solutes, formation of intrinsic *electronic* defects, oxidation and reduction, and defect association and precipitation. We now discuss some of these processes as further examples of defect chemical reactions.

Solute Incorporation. Solutes may enter solid solution in crystals as either substitutional or interstitial species. A simple example of a substitutional solute is NiO in MgO; the two form a complete solid solution (see Fig. 4.2). The defect chemical reaction for the dissolution of NiO in MgO is



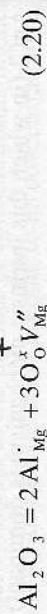
and involves no charged species.

Allovalent solutes greater or lesser in valence than the host on the other hand, must be charge-compensated in solid solution. This can occur by the formation of additional ionic defects or by liberating electrons and holes. The former is termed ionic compensation; the latter electronic compensation. The two types of compensation are related by oxidation/reduction equilibria, as discussed later with respect to electronic disorder (cf. Eqs. 2.54 and 2.55). Here we will introduce ionic compensation mechanisms.

Consider the dissolution of Al_2O_3 in MgO . Based on the similarity in ionic radii between Al^{3+} and Mg^{2+} in six-fold coordination (see Table 1.2) we may presume that the aluminum will substitute for magnesium. The oxygen ions are likely to occupy additional oxygen lattice sites. We at this point have



which accounts for all of the mass involved. However, we have satisfied neither site nor charge balance. The basis crystal for this solid solution is MgO , which has a 1:1 cation-anion stoichiometry, yet we have just created a 2:3 site ratio. By adding an additional vacant magnesium site, we can correct the situation:

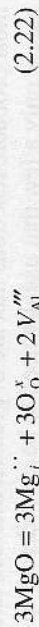


and at the same time satisfy charge balance. (One can also think of Eq. 2.20 as the extension of the crystal by three MgO formula units, in which two of the three new magnesium sites are occupied by aluminum and one is vacant.)

As a third example, consider the incorporation of MgO into Al_2O_3 . In this instance, the Mg ions may enter the solid solution substitutionally or interstitially; it is not exactly clear which is the lower energy option. If it is substitutional, a possible reaction is



and if it is interstitial, we can write:



A third possibility is that magnesium is *self-compensating* and forms both the interstitial and substitutional defect:



The reader should confirm that mass, site, and charge balance is maintained in each of these instances. Eqs. 2.21-2.23 are *limiting cases*, however, and if the respective energies are similar, no single one will be the dominant mechanism of incorporation. In analogy to chemical equilibria, Eqs. 2.21-2.23 represent chemical reactions that are simultaneously in equilibrium. Experimental data and calculations of the relative energies for these incorporation mechanisms suggest that at high temperatures magnesium is self-compensated (Eq. 2.23) to a large extent,

but that some minor compensation by cation vacancies or oxygen interstitials also exists. That is, the net incorporation reaction can be considered to be mostly reaction 2.23, plus some fraction of reactions 2.21 or 2.22.

Using these examples, we also emphasize that the free energy of solution for aliovalent solutes also includes the formation energy of the charge-compensating defects. Although Mg^{2+} and Al^{3+} are relatively close in ionic size, and can exchange for one another with little energy expenditure when both are present in a spinel (see Chapter 1), the energy of forming vacancies and interstitials constitutes a large fraction of the total energy for incorporation according to mechanisms such as 2.20-2.23.

Electrons, Holes, and Defect Ionization. In Kröger-Vink notation, free electrons and electron holes do not themselves occupy lattice sites. The process of forming intrinsic electron-hole pairs is excitation across the bandgap, which can be written as the "intrinsic electronic" reaction:



and for which the formation energy is the band gap of the material. An equilibrium constant may also be written for this reaction. The quantitative evaluation of electron and hole concentrations is discussed later.

When electrons and holes are tightly bound to an ion, or otherwise localized ("trapped") at a lattice site, the whole is considered to be one ionic defect. Thus the valence state of defects such as vacancies and interstitials can vary, in analogy to the valence of a transition metal ion ($\text{Fe}^{\times}_{\text{Mg}}$, Fe_{Mg}). For instance, an oxygen vacancy can in principle take on different valence states (V^{\times}_O , V^{\cdot}_O , $V^{\cdot\cdot}_\text{O}$), as can cation interstitials (for instance, $\text{Zn}^{\cdot}_\text{i}$ and $\text{Zn}^{\cdot\cdot}_\text{i}$ in the wurtzite structure compound ZnO). At a given temperature, one valence state is often much more prevalent than the others. Changes in valence take place via ionization reactions such as:



or:



for which equilibrium constants can be written:

$$K_1 = \frac{[V^{\cdot}_\text{O}]}{[V^{\cdot\cdot}_\text{O}]n} = \exp\left(-\frac{\Delta g_1}{kT}\right) \quad (2.27)$$

$$K_2 = \frac{[\text{Zn}^{\cdot\cdot}_\text{i}]}{[\text{Zn}^{\cdot}_\text{i}]p} = \exp\left(-\frac{\Delta g_2}{kT}\right) \quad (2.28)$$

The energies for these reactions Δg_1 , Δg_2 are effectively the ionization energies of the defect.