

CHAPTER 6

ELECTRICAL CONDUCTIVITY

INTRODUCTION

In the preceding chapter we have described and discussed diffusion of particles in solids and particularly of ions and defects in metal oxides. The driving force for the diffusion has been taken to be the negative value of the particle gradient or more precisely the negative value of the chemical potential gradient. When using isotopes as tracers one may study self-diffusion, i.e. diffusion of the components in the oxide (metal and oxygen ions) in a homogeneous oxide; in this case the isotopic tracer gradient is the driving force for the diffusion.

In this chapter the transport of electrical charges will be described and discussed. In metal oxides the electrically charged particles comprise ions and electrons. The ionic charge carriers comprise the cations, anions, and foreign ions (e.g. impurity ions, dopant ions and protons) and the electronic charge carriers are the electrons and electron holes. The concentrations of the charge carriers are directly related to the defect structure of the oxide and in this chapter we will derive expressions for the temperature and oxygen pressure dependence of the electrical conductivity. The discussion will be limited to transport of charges in chemically homogeneous metal oxides (no chemical potential gradient) but with an electrical potential gradient as the driving force. In the next chapter transport of ionic and electronic charge carriers in metal oxides which are simultaneously exposed to chemical and electrical potential gradients, i.e. electrochemical potential gradients, will be discussed.

As the mobilities of electrons and electrons holes are normally much higher than those of ions, most oxides are electronic conductors. One type of charge carrier often predominates in an oxide under particular conditions of temperature and oxygen pressure. An electronically conducting oxide is an n-conductor if transport of electrons predominate and a p-conductor if electron holes prevail. However, some oxides are or may become ionic conductors or mixed ionic/electronic conductors depending on the temperature and oxygen pressure often as a result of appropriate doping with aliovalent foreign ions. Some oxides may also exhibit proton conductivity in hydrogen- or water vapour-containing atmospheres; predominant proton conductivity in such oxides is in some cases observed at reduced temperatures ($< 600\text{-}700$ °C).

TRANSPORT IN AN ELECTRICAL POTENTIAL GRADIENT

As described in the previous chapter on diffusion in metal oxides the driving force is given by the negative of the potential gradient. The force exerted on a charged particle of type i with charge $z_i e$ is given by

$$F = -z_i e \frac{d\phi}{dx} = z_i e E \quad (6.1a)$$

where ϕ is the electrical potential and $E = -\frac{d\phi}{dx}$ is termed the electric field.

The flux of particles of type i is the product of the concentration c_i , the particle mobility B_i , and the force F :

$$j_i = c_i B_i F = z_i e c_i B_i E \quad (6.1b)$$

The current density I_i is given by the product of flux and charge:

$$I_i = z_i e j_i = (z_i e)^2 B_i c_i E \quad (6.2)$$

While B_i is the particle mobility ("beweglichkeit"), the product of B_i and the charge on each particle, $z_i e$, is termed the charge carrier mobility u_i :

$$u_i = z_i e B_i \quad (6.3)$$

Equation 6.2 can then be written

$$I_i = z_i e c_i u_i E = \sigma_i E \quad (6.4)$$

where $\sigma_i = z_i e c_i u_i$ is the electrical conductivity due to the charge carriers of type i . The electrical conductivity is determined by the product of the concentration c_i of the charged particles, the charge $z_i e$ on the particles and the charge carrier mobility, u_i . It should be noted that Eq.6.4 is an expression of Ohm's law. The unit for the electrical conductivity is Siemens per cm, Scm^{-1} (one Siemens is the reciprocal of one ohm and in older literature the electrical conductivity is expressed as $\text{ohm}^{-1}\text{cm}^{-1}$). The unit for the charge is coulomb, the concentration of charge carriers is expressed as the number of charge carriers of type i per cm^3 , and charge carrier mobility in units of cm^2/Vs . (Although the SI unit for length is m, cm is being used in the following as it is still by far the one most commonly used in the literature).

It may be noted that in the above terminology, F , E , I_i , z_i , u_i and j_i may each be positive or negative. u_i and z_i always have the same sign, and as long as no other forces than the the electrical act, I_i and E_i always have the same sign, and j_i and F always have the same sign. B_i and σ_i are always positive, and it is common also to neglect the sign when specifying charge carrier mobilities u_i .

The total electrical conductivity σ of a substance is the sum of the partial conductivities σ_i of the different charge carriers:

$$\sigma = \sum_i \sigma_i \quad (6.5)$$

The ratio of the partial conductivity σ_i to the total conductivity σ is termed the transport (or transference) number of species i :

$$t_i = \frac{\sigma_i}{\sigma} \quad (6.6)$$

Charge carriers in oxides.

The native charge carriers in a binary oxide are the cations, anions, electrons, and electron holes. The total conductivity is then given by

$$\sigma = \sigma_c + \sigma_a + \sigma_n + \sigma_p \quad (6.7)$$

where σ_c , σ_a , σ_n , and σ_p are the cation, anion, electron and electron hole conductivities, respectively.

Following Eq.6.6 the individual conductivities may be written in terms of their transport numbers: $\sigma_c = t_c \sigma$, $\sigma_a = t_a \sigma$, $\sigma_n = t_n \sigma$ and $\sigma_p = t_p \sigma$. Using these values Eq.6.7 takes the form

$$\sigma = \sigma (t_c + t_a + t_n + t_p) \quad (6.8)$$

It may be noted that the sum of the transport numbers of all the charge carriers equals unity: $t_c + t_a + t_n + t_p = 1$

The total electrical conductivity is often given by the sum of the ionic conductivity, $\sigma_{ion} = \sigma_c + \sigma_a$, and the electronic conductivity, $\sigma_{el} = \sigma_n + \sigma_p$, and the total conductivity can then be written

$$\sigma = \sigma_{\text{ion}} + \sigma_{\text{el}} \quad (6.9)$$

Often only one type of charge carrier dominates the charge transport, and in many cases and as an approximation contributions from minority carriers are neglected. For oxides the mobilities of electrons and electron holes are usually several orders of magnitude ($\sim 10^4 - 10^8$) larger than those of the ions, and even when the concentration of electron or electrons holes is smaller than that of the ionic charge carriers (or, more precisely, than that of ionic charge carrier defects) the oxide may still be a predominantly electronic conductor. The relative importance of ionic and electronic conductivity will often vary greatly with temperature and oxygen pressure. This will be illustrated in the following chapters.

The Nernst-Einstein equation: Relation between the mobility and diffusion coefficient.
In the previous chapter it was shown that the relation between the random diffusion coefficient of particles of type i and the particle mobility is given by

$$D_i = kTB_i$$

By combining this relation with Eqs.6.3 and 6.4 one obtains the following relation between the random diffusion coefficient and the charge carrier mobility and the electrical conductivity:

$$D_i = u_i \frac{kT}{z_i e} = \sigma_i \frac{kT}{c_i z_i^2 e^2} \quad (6.10)$$

This relation is called the Nernst-Einstein relation.

This relation and also the effect of an applied electric field on migration of charged species in a homogeneous crystal may also be derived from the following model.

Consider a one-dimensional system with a series of parallel planes separated by a distance s (cf. Fick's first law in Chapter 5). It is assumed that the system is homogeneous and that the volume concentration of the particles in the planes is c_i . The particles in neighbouring planes 1 and 2 have equal probability of jumping to the neighbouring planes. In the absence of any external kinetic force, the number of particles which jump from plane 1 to plane 2 and from 2 to 1 per unit time is equal and opposite and given by $\frac{1}{2} \omega c_i s$. In a homogeneous system there will be no net transport of particles.

When there is no applied electric field, the activation energy associated with the jumps is ΔH_m . When an electric field E is applied, the jump frequency in the positive direction will be increased and that in the negative direction decreased in that the activation energies are changed. In the forward direction the activation energy is reduced to $\Delta H_m - \frac{1}{2} z_i e s E$ and in the reverse direction increased to $\Delta H_m + \frac{1}{2} z_i e s E$. This is illustrated schematically in Fig.6.1.

The net particle flux is given by the difference in number of jumps in the forward and reverse directions:

$$j_i = \frac{1}{2} c_i s \{ \omega_{\text{forw}} - \omega_{\text{rev}} \} \quad (6.11)$$

where

$$\omega_{\text{forw}} = v \exp\left(\frac{\Delta S_m}{k}\right) \exp\left(-\frac{\Delta H_m - \frac{z_i e s E}{2}}{kT}\right)$$

and

$$\omega_{\text{rev}} = v \exp\left(\frac{\Delta S_m}{k}\right) \exp\left(-\frac{\Delta H_m + \frac{z_i e s E}{2}}{kT}\right).$$

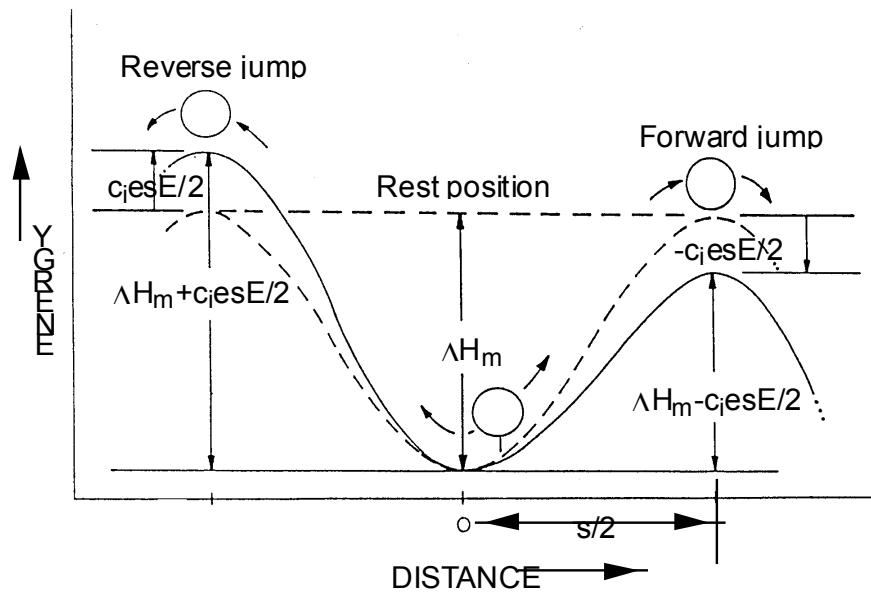


Fig.6.1 Schematic illustration of the effect of an electric field on the migration of charged species in a homogeneous crystal. E represents the electric field. ΔH_m is the activation energy in the absence of an electric field. In the forward direction the activation energy may be considered to be lowered by $\frac{1}{2} z_i e s E$ and increased by the same amount in the reverse direction.

Equation 6.11 then becomes

$$j_i = \frac{1}{2} c_i s \omega \left\{ \exp\left(\frac{z_i e s E}{2kT}\right) - \exp\left(-\frac{z_i e s E}{2kT}\right) \right\} \quad (6.12)$$

where $\omega = v \exp\left(\frac{\Delta S_m}{k}\right) \exp\left(-\frac{\Delta H_m}{kT}\right)$.

When $z_i e s E \ll 2kT$, which is valid for all normal electrical measurements in bulk materials (and when Ohm's law is applicable) then the difference in exponentials in Eq.6.12 may be written $z_i e s E/kT$ (since $e^x - e^{-x} = 2x$ for $x \ll 1$). Eq.6.12 then takes the form

$$j_i = \frac{1}{2} \omega s^2 c_i \frac{z_i e E}{kT} \quad (6.13)$$

The diffusion coefficient for one-dimensional random diffusion is given by $D_i = \frac{1}{2} \omega s^2$ and j_i then becomes

$$j_i = D_i \frac{c_i z_i e E}{kT} \quad (6.14)$$

As we have shown before, the flux of particles with a charge $z_i e$ may also be expressed in terms of particle or charge carrier mobilities or conductivity:

$$j_i = z_i e c_i B_i E = c_i u_i E = \frac{\sigma_i E}{z_i e} \quad (6.15)$$

and when one combines Eqs.6.14 and 6.15 one obtains various forms of the Nernst-Einstein relation (Eq.6.10)

$$D_i = B_i kT = u_i \frac{kT}{z_i e} = \sigma_i \frac{kT}{c_i z_i e^2} \quad (6.10)$$

It is emphasised that the relation is derived assuming random diffusion and that the mobilities and conductivity through this relation connects to the random (or self) diffusion coefficient D_r . It is thus meaningful for relating electrical and diffusional transport of atoms and ions. For electrons and holes this is only meaningful when they migrate by an activated hopping mechanism.

From the Nernst-Einstein relation it is also seen that the temperature dependence of the product $\sigma_i T$ is the same as that of D_r . Thus in evaluating the activation energy associated with the diffusion coefficient from conductivity measurements, it is necessary to plot $(\sigma_i T)$ vs $1/T$.

It is also important to note that in the derivation it is implicitly assumed that the ions and electrons move independently of each other, i.e. that there is no interference between ionic and electronic flows. In the literature this has generally been assumed to be the case, but recent studies - so far mainly on CoO - have shown that this is not necessarily the case. This will be further discussed in the chapter on the properties of CoO.

ELECTRONIC CONDUCTIVITY IN OXIDES

Most metal oxides are electronic conductors at high temperatures. For many of these oxides the conductivity increases with increasing temperature and as the conductivity at the same time is much smaller than in metals, this type of conductivity is termed semiconductivity. The principal reason for the increasing conductivity is that the number of electronic defects increases with increasing temperature. A limited number of oxides - especially among transition metal monoxides - are metallic conductors and for which the conductivity decreases with increasing temperature. In this case this is attributed to a mobility of electronic defects decreasing with increasing temperature. Other oxides, e.g. p-conducting acceptor-doped perovskites to be discussed in a later chapter, also exhibit metallic-like conductivity in that the conductivity also here decreases with increasing temperature; however in these cases the decreasing conductivity is attributed to a decreasing number of electron holes with increasing temperature, and the conductivity is thus not to be classified as metallic.

The electronic conductivity, σ_{el} , of a semiconducting oxide is given by

$$\sigma_{el} = \sigma_n + \sigma_p = enu_n + epu_p \quad (6.16)$$

where σ_n and σ_p are the electron and electron hole conductivities, n and p the charge carrier concentrations of electrons and electron holes, respectively, and u_n and u_p are the carrier (or drift) mobilities of electrons and electron holes. As mentioned above, one type of charge

carrier will often dominate; however, in special cases where an oxide is close to stoichiometric both n- and p- conductivity may contribute significantly to the electronic conductivity.

In defect-chemical equations the concentrations of electrons and electron holes are often written in terms of the law of mass action without specifying where the electronic defects are located. The concentrations of electronic defects are often interpreted in terms of the band theory of solids and in the following is given a brief account of this theory and the relationship between this theory and the law of mass action.

THE BAND THEORY

In single atoms the electrons may only possess discrete energies. These allowed energies are designated by quantum numbers which refer to the electron shell which the electron occupies (the principal quantum number), the orbital angular momentum of the electron (azimuthal quantum number), and the direction of the angular momentum vector (magnetic quantum number). In addition, and according to the Pauli exclusion principle, each energy state can only be accommodated by two electrons which have opposite spins.

When individual atoms are brought together in a solid, i.e. when interatomic spacing decreases and electronic levels overlap, a splitting of the energy levels begin to occur, and the energy levels may be considered to form energy bands in the solid. But the total number of levels within a band corresponds exactly to the total number of atoms present in the solid, and therefore the levels become more and more finely spaced the larger the number of atoms present. Because of the Pauli exclusion principle, each band can accommodate twice as many electrons as there are energy levels. Solids contain 10^{22} - 10^{23} atoms per cm^3 , and the number of levels in each band is thus of the same order.

The energy bands may overlap or be separated by energy gaps. At absolute zero temperature (0 K) the electrons fill up the lowest possible energy levels. The highest filled band represents the orbitals of valence electrons and is termed the valence band. It is completely filled at 0 K while the next band, termed the conduction band is completely empty. In Fig.6.2, where the vertical axis represents the electron energy and horizontal axis the distance through the solid, the valence and conduction bands are separated by an energy gap, as is the case in semiconductors and insulators. In a pure, perfect and ideal solid the electrons may not possess energies within the energy gap, and this is therefore also often termed the forbidden energy gap. The size of the energy gap differs for inorganic compounds, and empirically it is found that the energy gap increases with the heat of atomisation of the compounds. For binary

semiconductors and insulators it has specifically been shown that the band gap, E_g (in electron volts) can be expressed approximately as

$$E_g = 2(E_s - c) \quad (6.17)$$

where $E_s = E_{at}/\text{equivalent}^*$ and c is a constant approximately equal to 2.7.

In materials where the valence band is only partly occupied or where it overlaps with the conduction band (no forbidden band gap) the electrons can move freely in the available energy levels and we have metallic conduction.

In an insulator or semiconductor at 0 K there is a band gap and the valence band is completely filled with electrons while the conduction band is completely empty. In such cases no electronic conduction takes place when an electric field is applied.

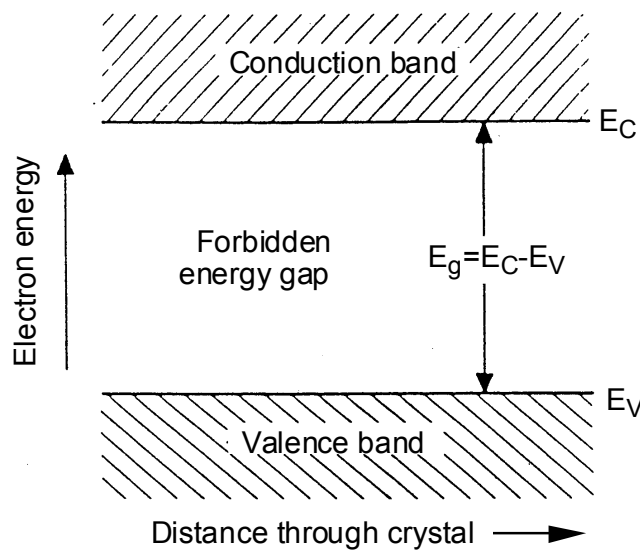


Fig.6.2. Schematic illustration of the energy band diagram for a pure semiconductor

Intrinsic ionisation. When the temperature is increased, electrons in the valence band are excited across the forbidden energy gap to the conduction band. This is the intrinsic ionisation. The electrons in the conduction band and the unoccupied electron sites in the valence band (electron holes) can move in an electric field. The electron holes behave as though they were positively charged and move in the opposite direction of the electrons. The intrinsic ionisation thus produces pairs of electron + electron hole charge carriers. When the

* An equivalent in M_aO_b is equal to $az_{cat} = b|z_{an}|$

electronic conductivity is due to intrinsic ionisation only, the semiconductor is called an intrinsic semiconductor. According to this model electron and electron hole conductivities increase with increasing concentrations of electrons in the conduction band and electron holes in the valence band.

In many oxides, and particularly those with large percentage ionic bonding, periodic fluctuations of the electric potential associated with each ion become too large (and energy bands too narrow) so that the band model provides an inadequate description or theory. In this case the electrons or holes may be considered to be localised at the lattice atoms. Such localised electronic defects are termed polarons and may from a chemical point of view be considered to constitute valence defects.

When classical statistics (the Boltzmann approximation) can be used it may be shown that the concentration of electrons and electron holes (expressed in number per cm³) is given by

$$n = N_C \exp\left(-\frac{E_C - E_F}{kT}\right) \quad (6.18)$$

$$p = N_V \exp\left(-\frac{E_F - E_V}{kT}\right) \quad (6.19)$$

N_C and N_V represent the number of available states (degeneracy or effective density of states) per unit volume in the conduction and valence bands. E_C is the energy of the lowest level of the conduction band and E_V the highest level in the valence band. The parameter E_F is termed the Fermi level and we will return to this later on.

When the electrons occupy a narrow band of energies close to E_C , a parabolic relation between N_C and E_C may be assumed and it may be shown that N_C is then given by

$$N_C = \left(\frac{8\pi m_e^* kT}{h^2} \right)^{3/2} \quad (6.20)$$

where m_e^* is the effective mass of the electron. When the holes occupy a narrow region of energies close to E_V , N_V is correspondingly given by

$$N_V = \left(\frac{8\pi m_h^* kT}{h^2} \right)^{3/2} \quad (6.21)$$

where m_h^* is the effective mass of the electron hole. The effective masses of electrons and electron holes are seldom accurately known and as an approximation the free electron mass is then used in these relations.

The defect reaction and corresponding equilibrium between electrons in the conduction band and electron holes in the valence band can in terms of the law of mass action be expressed as

$$0 = e' + h' \quad (6.22)$$

$$n \cdot p = K_i \quad (6.23)$$

where K_i is the equilibrium constant for the intrinsic ionisation. Combination with Eqs. 6.18 and 6.19 gives

$$K_i = n \cdot p = N_C N_V \exp\left(-\frac{E_g}{kT}\right) \quad (6.24)$$

where E_g is the band gap, $E_g = E_C - E_V$. E_g may thus be considered the enthalpy of the intrinsic ionisation. It is emphasised that Eq.6.18 presupposes that classical statistics apply. It may also be noted that the Fermi level is eliminated in this expression of the law of mass action. It may be noted again that in Eq. 6.24 the concentrations of electrons and electron holes are expressed in terms of number per volume unit (e.g. per cm^3).

Intrinsic electronic semiconductor. In an intrinsic semiconductor the concentrations of electrons and electron holes are equal, and thus

$$n = p = K_i^{1/2} = (N_C N_V)^{1/2} \exp\left(-\frac{E_g}{2kT}\right) \quad (6.25)$$

and the electronic conductivity (Eq.6.16) then becomes

$$\sigma_{el} = \sigma_n + \sigma_p = en\mu_n + ep\mu_p = e (N_C N_V)^{1/2} (u_n + u_p) \exp\left(-\frac{E_g}{2kT}\right) \quad (6.26)$$

It may be noted that N_C and N_V are temperature dependent and that also u_n and u_p may have various dependencies on temperature. If the latter are not exponential (as in diffusional hopping conduction processes) the exponential term of the energy gap tend to dominate the temperature dependence and as an approximation Eq.6.26 is then often written

$$\sigma_{el} = \text{const.} \exp\left(-\frac{E_g}{2kT}\right) \quad (6.27)$$

From these relations it is evident that the intrinsic electronic conductivity increases with decreasing energy gap.

Effects of charged impurities or defects. Extrinsic semiconductors. As stated before, the valence and conduction bands may be considered to constitute the highest filled orbital and the lowest empty orbital, respectively. The valence band may in an oxide typically represent the 2p states of the O^{2-} ions, and removing an electron from here (creating a hole) may be regarded as the creation of an O^- ion, which is intuitively possible. The conduction band typically represents the reduced state of a metal constituent ion. For instance, in oxides with Ti^{4+} such as TiO_2 or $SrTiO_3$ the conduction band would typically represent the 4s state of the Ti^{3+} ion. The size of the band gap can be imagined to represent the difficulty of simultaneously oxidising O^{2-} to O^- and reducing Ti^{4+} to Ti^{3+} . In the chosen example we expect a moderate band gap. Similar oxides with Mn^{4+} would be more easily reducible and have smaller band gaps, while oxides with Si^{4+} or Zr^{4+} are less easily reducible and have larger band gaps.

Let us now consider the addition of small amounts of imperfections or impurities. These may be considered to contribute additional localised energy levels in the crystal. It is commonly assumed that these always fall within the forbidden gap. As we shall see later on this leads to situations where a certain temperature is needed to excite these defects to become effectively charged. This is not in accordance with experimental evidence and is not intuitive for imperfections with very stable aliovalent valence states. Thus, we will first consider cases where imperfections introduce levels outside the forbidden gap.

If these levels fall below the valence band edge E_V they will always be occupied (even at 0 K) and be in a reduced state. We refer to it as an acceptor imperfection. For instance, Al^{4+} substituting Ti^{4+} in the abovementioned oxides may always be considered to be reduced to Al^{3+} and as such be a charged defect even at 0 K, for instance taking the electron from the valence band. We may draw this conclusion from the higher stability of O^- as compared to Al^{4+} .

Similarly, an imperfection introducing a level above the conduction band edge E_C may always be considered to lose its electron and be oxidised even at 0 K. We refer to it as a donor. For instance, La^{2+} substituting Sr^{2+} and possibly Ta^{4+} substituting Ti^{4+} would be

oxidised to La^{3+} and Ta^{5+} by giving off the electron to the easier formed Ti^{3+} of the conduction band.

The above examples lead to compensating electronic defects even at 0 K, but real cases may comprise simultaneous formation of point defects that may annihilate the electronic defects, (depending on oxygen activity). Thus, while Ca substituting La in LaCrO_3 is compensated by electron holes at high oxygen partial pressures, Al or Ta substituting Ti in SrTiO_3 will be compensated by oxygen vacancies or metal vacancies, respectively, under the same conditions. Of course, this brings up a question of whether native point defects such as vacancies at different stages of ionisation themselves introduce levels within or outside the band gap. If aliovalent dopants charged at 0 K are to be compensated by point defects at 0 K, these point defects must themselves be charged at 0 K and thus have levels outside the band gap.

In the following we consider imperfections introducing levels inside the forbidden energy gap as illustrated in Fig.6.3. When the imperfection introduces an energy level which is located

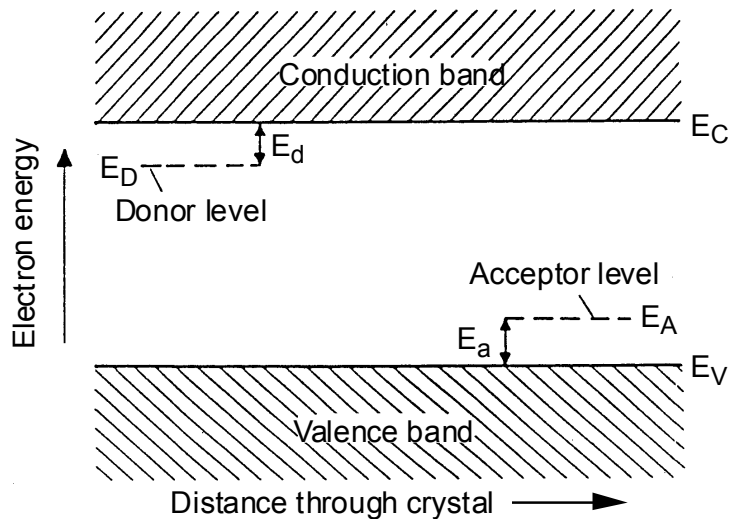


Fig.6.3 Schematic illustration of additionally localised energy levels due to donors and acceptors in the forbidden energy gap in the energy band diagram of a semiconductor.

below the lower edge of the conduction band (E_C), electrons can be thermally excited to the conduction band. As such the imperfection donates an electron, it is called a donor and the corresponding energy level a donor level. Under conditions where such imperfections dominate the defect structure the oxide becomes an n-conductor. Correspondingly, imperfections with energy levels just above the upper edge of the valence band (E_V) are termed acceptors; electrons in the valence band may be excited to the energy level of the imperfection (acceptor level) and the oxide may become a p-conductor.

In SrTiO₃ it is for instance found that Fe⁴⁺ substituting Ti⁴⁺ is an acceptor inside the gap; Fe³⁺ (the result after acceptance of an electron) is less favourable than Fe⁴⁺ (when the electron is taken from O²⁻) and at a higher energy than the valence band of the O²⁻ electrons, but Fe³⁺ is clearly more favourable than Ti³⁺ and thus way below the conductance band. Similarly, oxygen vacancies are considered to be donors in the gap, and this can be viewed as a trapping of electrons at Ti⁴⁺ (as Ti³⁺) near the vacancy.

While donors and acceptors inside the forbidden gap have positive energies of ionisation, the donors and acceptors outside the gap may be considered simply to have negative energies of ionisation.

Effects of donors. Let us again describe these processes in terms of the law of mass action. Thus the ionisation of a donor D^x may be written



and the corresponding equilibrium by

$$\frac{[D^\cdot]n}{[D^x]} = K_D \quad (6.29)$$

If the total number of donors is N_D, then

$$N_D = [D^\cdot] + [D^x] \quad (6.30)$$

If the energy of the donor state is E_D, and the donor state is mainly empty ([D^x] << N_D) then the concentration of electrons in the donor state, [D^x], may following Boltzmann statistics (be expressed by

$$[D^x] = N_D \exp\left(-\frac{(E_D - E_F)}{kT}\right) \quad (6.31)$$

Since we assume $\frac{[D^x]}{N_D} \ll 1$, and that Boltzmann statistics also apply to conduction band electrons and by further combining Eqs.6.18 and 6.29-6.31, we get an expression for K_D:

$$K_D = N_C \exp\left(-\frac{E_C - E_D}{kT}\right) = N_C \exp\left(-\frac{E_d}{kT}\right) \quad (6.32)$$

where $E_d = E_C - E_D$ represents the ionisation energy of the donor (cf. Fig.6.3). E_d may in Eq.6.32 be considered to be the enthalpy of the ionisation of the donor.

When no other imperfections are present, the situation described here can be approximated by

$$n = [D^\cdot] \approx N_D \quad (6.33)$$

and if the donors are present in an invariable amount as a fully soluble or frozen-in impurity, then $n = [D^\cdot] \approx N_D = \text{constant}$. From Eq. 6.29, we then get the minority concentration of neutral unionised donors: $[D^x] = N_D^2 N_C^{-1} \exp(+E_d/kT)$.

If, on the other hand the donor level is mainly unionised, then $[D^\cdot] \ll [D^x] \approx N_D$ and Boltzmann statistics give

$$[D^\cdot] = N_D \exp\left(-\frac{E_F - E_D}{kT}\right) \quad (6.34)$$

and then, by combination with Eqs. 6.18, 6.29, and 6.30 we again obtain $K_D = N_C \exp(-E_d/kT)$ as in Eq.6.32.

If the electroneutrality condition in the oxide is still given by

$$n = [D^\cdot] \quad (6.35)$$

(but now $[D^\cdot] \ll N_D$), then the concentration of electrons is, from insertion in Eq.6.29:

$$n = [D^\cdot] = (K_D N_D)^{1/2} = (N_C N_D)^{1/2} \exp\left(-\frac{E_d}{2kT}\right) \quad (6.36)$$

The reader may find it useful to note the similarity between the form of this expression and Eq.6.25. However, we also remind ourselves that N_D may be a constant concentration of impurities or a constant or varying level of other point defects such as anion vacancies or cation interstitials.

In the above we have seen that the same equilibrium constant K_D for Eq. 6.28 applies whether the donor level is approximately empty (fully ionised) or approximately fully occupied (practically unionised, or, in this case, neutral). But our treatment does not hold for intermediate situations, i.e. what we may call partly filled donor levels. In the latter case

Boltzmann statistics do not represent a sufficiently good approximation, and instead Fermi-Dirac statistics must be used.

Let us recapitulate briefly the treatment of the ionisation of a constant concentration of a donor in the forbidden gap of an otherwise pure, stoichiometric, ideal semiconductor: At low temperatures, the concentration of electrons is given by a minor degree of ionisation of the donors, as given by Eq.6.36. If we neglect the temperature dependence of N_C , the situation can be illustrated as in the right-hand part of Fig. 6.4; the concentration of electrons increases with an apparent enthalpy of $E_d/2$. At a sufficiently high temperature (middle part of Fig. 6.4) all donors are ionised, and the concentration of electrons becomes constant (Eq.6.33). At even higher temperatures intrinsic semiconduction may predominate, i.e., $n = p$, and in principle the temperature dependence becomes as illustrated in the left hand part of Fig.6.4, with an apparent enthalpy close to $E_g/2$ (cf. Eq.6.25). Thus at low temperatures this oxide is an n-conductor due to the ionisation of the donors and at high temperatures intrinsic ionisation predominates. The behaviour over the entire temperature range could in principle be solved from the full electroneutrality equation

$$n = [D'] + p \tag{6.37}$$

in combination with the constancy of the donor concentration and the expressions for the equilibrium constants K_i (Eq.6.24) and K_D (Eq. 6.32). However, as noted above, the expression for K_D would not be valid between the intermediate and low temperature (right hand side) domains in Fig. 6.4.

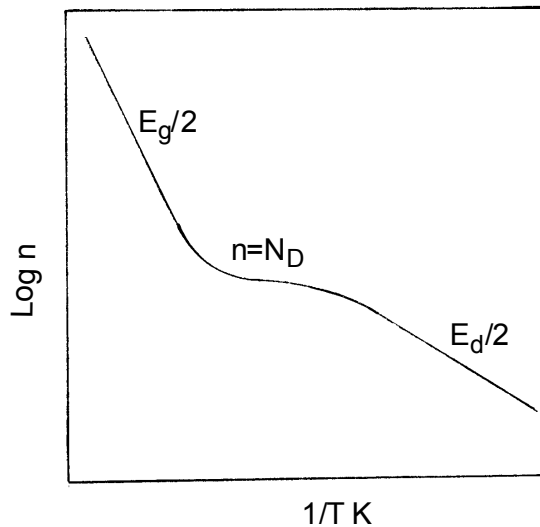


Fig.6.4 Schematic illustration of the logarithm of the concentration of defect electrons as a function of the reciprocal absolute temperature for a semiconductor with donors.

Effects of acceptors. A corresponding treatment may be made for ionisation of acceptors, which in terms of a defect reaction may be written



The equilibrium constant for the defect reaction is given by

$$\frac{[A']p}{[A^x]} = K_A \quad (6.39)$$

Following a similar treatment as for the donor, K_A may under the assumption that Boltzmann statistics apply to the valence band (small concentration of holes) and the acceptor (nearly full or nearly empty acceptor levels) be expressed by

$$K_A = N_V \exp\left(-\frac{E_A - E_V}{kT}\right) = N_V \exp\left(-\frac{E_a}{kT}\right) \quad (6.40)$$

where E_A is the energy level of the acceptor and $E_a = E_A - E_V$ is called the ionisation energy of the acceptor (cf. Fig.6.3).

For an acceptor doped oxide the temperature dependence of the concentration of holes will be qualitatively analogous to that of electrons in the donor doped case (cf. Fig. 6.4) with the same constrictions.

The Fermi level and chemical (or electrochemical) potential of electrons.

In this chapter we have so far treated the defect equilibria for semiconductivity in terms of the band model. In this model one makes use of the parameter termed the Fermi level, E_F . As the defect equilibria are otherwise described by equilibrium thermodynamics, it is of interest to correlate the band model with the thermodynamic approach.

A chemical equilibrium implies that the chemical potential of a species is the same in all phases. As regards electrons in a system, this also means that their chemical potentials (or electrochemical potentials if the inner potential can not be neglected) must be equal, although they may have different energies. Thus the chemical potential of the electrons in general, μ_e , must be equal to the chemical potential of valence electrons, conduction electrons, etc.,

$$\mu_e = \mu(\text{cond. electrons}) = \mu(\text{valence electrons}) \quad (6.41)$$

The chemical potential of electrons, for instance, the conduction electrons, may be written in terms of the chemical potential in a standard state, $\mu^\circ(\text{cond. electrons})$ and a term for the entropy of mixing:

$$\mu_e = \mu(\text{cond. electrons}) = \mu^\circ(\text{cond. electrons}) + kT \ln \frac{n}{N_C} \quad (6.42)$$

From the relation between the concentration of conduction electrons, n , the conduction band energy level E_C and the Fermi level E_F (Eq.6.18) we may write

$$E_F = E_C + kT \ln \frac{n}{N_C} \quad (6.43)$$

By comparing Eqs. 6.42 and 6.43 it is seen that if E_C is considered to be the chemical potential in the standard state for conduction electrons, the Fermi level represents the chemical potential of the conduction electrons, and thus of all electrons in a substance.

CHARGE CARRIER MOBILITIES OF ELECTRONS AND ELECTRON HOLES.

In the preceding chapters we have looked at temperature dependencies of concentrations of electronic defects and point defects, and we have looked at the conductivity and mobility of thermally activated diffusing species. In the following we consider the charge carrier mobilities of electrons and holes in some more detail. For instance for an intrinsic electronic semiconductor (where $n=p$) we can from Eq. 6.26 in combination with Eqs.6.20 and 6.21 write an expression for σ_{el} :

$$\sigma_{el} = \{2e \left(\frac{2\pi k}{h^2} \right)^{3/2} (m_e^* \cdot m_h^*)^{3/4} T^{3/2} \exp \left(-\frac{E_g}{2kT} \right)\} (u_n + u_p) \quad (6.44)$$

The effective mass of electrons and electron holes can be interpreted by a quantum mechanical treatment of electronic motion of electrons and electron holes in solids. The effective mass differs from the real mass of electrons due to the interaction of electrons with the periodic lattice of the atoms. Only for a completely free electron is the mass equal to the real mass, $m_e = m_e^*$. As mentioned above, the values of the effective masses are not accurately known, and the value of m_e is often used as an approximation.

In order to obtain an accurate description of the temperature dependence of the electronic conductivity it is necessary to consider the temperature dependencies of the charge carrier mobilities.

Non-polar solids. The temperature dependence of the charge carrier mobility is dependent on the electronic structure of the solid. For a pure non-polar semiconductor - as in an ideal and pure covalent semiconductor - the electrons in the conduction band and the electron holes in the valence band can be considered as quasi-free particles. Then the mobilities of electrons and electron holes, u_n and u_p , are determined by the thermal vibrations of the lattice in that the lattice vibrations result in electron and electron hole scattering (lattice scattering). Under these conditions the charge carrier mobilities of electrons and electron holes are both proportional to $T^{-3/2}$, e.g.

$$u_{n,latt} = \text{const. } T^{-3/2} \quad (6.45)$$

In this case the temperature dependence of σ_{el} (Eq.6.44) becomes

$$\sigma_{el} = \text{const. } T^{3/2} \cdot T^{-3/2} \exp\left(-\frac{E_g}{2kT}\right) = \text{const. } \exp\left(-\frac{E_g}{2kT}\right) \quad (6.46)$$

If, on the other hand, the scattering is mainly due to irregularities caused by impurities or other imperfections, the charge carrier mobility is proportional to $T^{3/2}$, e.g.

$$u_{n,imp} = \text{const. } T^{3/2} \quad (6.47)$$

If both mechanisms are operative, the mobility is given by

$$u = \frac{1}{\frac{1}{u_{latt}} + \frac{1}{u_{imp}}} \quad (6.48)$$

and from the temperature dependencies given above it is evident that impurity scattering dominates at low temperature while lattice scattering takes over at higher temperature.

Polar oxides. When electrons and electron holes move through polar oxides, they polarise the neighbouring lattice and thereby cause a local deformation of the structure. Such an electron or electron hole with the local deformation is termed a polaron. The polaron is considered as a fictitious single particle.

When the interaction between the electron or electron hole and the lattice is relatively weak, the polaron is referred to as a large polaron. Large polarons behave much like free carriers except for an increased mass caused by the fact that polarons carry their associate deformations. Large polarons still move in bands, and the expressions for the effective density

of states in the valence and conduction bands are valid. The temperature dependence of the mobilities of large polarons at high temperatures* is given by

$$\mu_{\text{large pol.}} = \text{const. } T^{-1/2} \quad (6.49)$$

For an intrinsic semiconducting oxide where the electronic conductivity mechanism can be described in terms of a large polaron mechanism, the temperature dependence of σ_{el} can be written by combination of Eqs. 6.44 and 6.49

$$\sigma_{\text{el}} = \text{const. } T \cdot \exp\left(-\frac{E_g}{2kT}\right) \quad (6.50)$$

Thus in this case the value of the band gap can be deduced by plotting $\log(\sigma_{\text{el}}/T)$ vs $1/T$.

The large polaron mechanism has been suggested for highly ionic non-transition metal oxides. Such oxides have large energy gaps ($E_g \geq 6 \text{ eV}$), where the band structure is characterised by large band widths. Due to the large band gap one expects electronic semiconductivity to predominate only at high temperatures in these oxides.

For other oxides it has been suggested that the interactions between the electronic defects and the surrounding lattice can be relatively strong and more localised. If the dimension of the polaron is smaller than the lattice parameter, it is called a small polaron or localised polaron, and the corresponding electronic conduction mechanism is called a small polaron mechanism.

The transport of small polarons in an ionic solid may take place by two different mechanisms. At low temperatures small polarons may tunnel between localised sites in what is referred to as a narrow band. The temperature dependence of the mobility is determined by lattice scattering and the polaron mobility decreases with increasing temperature in a manner analogous to a broad band semiconductor.

However, at high temperatures (for oxides $> \sim 500 \text{ }^\circ\text{C}$) the band theory provides an inadequate description of the electronic conduction mechanism. The energy levels of electrons and electron holes do not form bands, but are localised on specific atoms of the crystal structure (valence defects). It is assumed that an electron or electron hole is self-trapped at a given lattice site, and that the electron (or electron hole) can only move to an adjacent site by an

* "High temperatures" are temperatures above the optical Debye temperature, θ . For oxides $\theta \sim (h\omega)/2\pi k$, where h is the Planck constant, k the Boltzmann constant and ω the longitudinal optical frequency which for an oxide is $\sim 10^{14} \text{ s}^{-1}$.

activated hopping process similar to that of ionic conduction. Consequently it has been suggested that the mobility of a small polaron can be described by a classical diffusion theory as described in a preceding chapter and that the Nernst -Einstein can be used to relate the activation energy of hopping, E_u , with the temperature dependence of the mobility, u , of an electron or electron hole:

$$u = \frac{e}{kT} D = \text{const. } T^{-1} \exp \left(-\frac{E_u}{kT} \right) \quad (6.51)$$

where E_u is the activation energy for the jump. In a more detailed treatment it has also been shown that for very strong interactions (so-called nonadiabatic case) the small polaron mobility can alternatively be written

$$u = \text{const. } T^{-3/2} \exp \left(-\frac{E_u}{kT} \right) \quad (6.52)$$

Both expressions have been used in the literature in interpretations of the small polaron mechanisms.

At high temperatures, the exponential temperature dependence of small polaron mobilities can thus in principle be used to distinguish it from the other mechanisms. The different mechanisms can also be roughly classified according to the magnitude of the mobilities; the lattice and impurity scattering mobilities of metals and non-polar solids are higher than large-polaron mobilities which in turn are larger than small-polaron mobilities.

Large polaron mobilities are generally of the order of $1-10 \text{ cm}^2/\text{V}^{-1}\text{s}^{-1}$, and it can be shown that a lower limit is approximately $0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

Small polaron mobilities generally have values in the range $10^{-4}-10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. For small polarons in the regime of activated hopping the mobility increases with increasing temperature and the upper limit is reported to be approximately $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

NONSTOICHIOMETRIC SEMICONDUCTORS.

Corresponding expressions for σ_{el} for nonstoichiometric electronic semiconductors readily follows by considering the temperature and oxygen pressure dependence of the concentration of the electronic defects.

For nonstoichiometric oxides the concentration of electronic defects is determined by the deviation from stoichiometry, the presence of native charged point defects, aliovalent impurities and/or dopants. The concentration of electronic defects can be evaluated from proper defect structure models and equilibria. Various defect structure situations have been described in previous chapters and at this stage only one example - dealing with oxygen deficient oxides with doubly charged oxygen vacancies as the prevalent point defects - will be described to illustrate the electrical conductivity in nonstoichiometric oxides.

Oxygen deficient oxides.

Let us recapitulate the equations for formation of doubly charged oxygen vacancies. As described in Chapter 3 the defect equation may be written



The corresponding defect equilibrium is given by

$$[\text{V}_\text{O}^{2\cdot}] n^2 = K_{\text{V}_\text{O}^{2\cdot}} p_{\text{O}_2}^{-1/2} \quad (6.54)$$

If we deal with a high-purity oxide where the concentration of impurities can be ignored compared to the concentration of oxygen vacancies and electrons, the electroneutrality condition becomes

$$n = 2[\text{V}_\text{O}^{2\cdot}] \quad (6.55)$$

By combining equations 6.54 and 6.55 the concentration of electrons is given by

$$n = 2[\text{V}_\text{O}^{2\cdot}] = (2K_{\text{V}_\text{O}^{2\cdot}})^{1/3} p_{\text{O}_2}^{-1/6} \quad (6.56)$$

The total electrical conductivity is given by the sum of the conductivity of the electrons and of the oxygen vacancies:

$$\sigma_t = 2 e [\text{V}_\text{O}^{2\cdot}] u_{\text{V}_\text{O}^{2\cdot}} + e n u_n \quad (6.57)$$

$2 e [V_O^{2\cdot}] u_{V_O^{2\cdot}}$ represents the ionic conductivity due to the oxygen vacancies and where $u_{V_O^{2\cdot}}$ is the mobility of the oxygen vacancies. However, if the electrons and oxygen vacancies are the prevalent charge carriers, the contribution due to oxygen vacancies can be ignored due to the much higher mobility of electrons than oxygen vacancies, and the oxide is an n-conductor where the conductivity can then be written

$$\sigma_t = \sigma_n = e n u_n = e u_n (2K_{V_O^{2\cdot}})^{1/3} p_{O_2}^{-1/6} \quad (6.58)$$

As described in previous chapters the equilibrium constant for the formation of doubly charged oxygen vacancies and 2 electrons is given by

$$K_{V_O^{2\cdot}} = \exp\left(\frac{\Delta S_{V_O^{2\cdot}}}{k}\right) \exp\left(-\frac{\Delta H_{V_O^{2\cdot}}}{kT}\right) \quad (6.59)$$

When one combines Eqs.6.58 and 6.59 the n-conductivity may be written:

$$\sigma_t = \sigma_n = e u_n \exp\left(\frac{\Delta S_{V_O^{2\cdot}}}{3k}\right) \exp\left(-\frac{\Delta H_{V_O^{2\cdot}}}{3kT}\right) p_{O_2}^{-1/6} \quad (6.60)$$

Let us further assume that the electrons are small polarons and thus that the mobility of the electrons are given by Eq.6.51. The conductivity can then be expressed by

$$\sigma_n = \text{const.} \frac{1}{T} \exp\left(-\frac{\Delta H_{V_O^{2\cdot}}/3 + E_u}{kT}\right) p_{O_2}^{-1/6} \quad (6.61)$$

Thus following this equation the n-conductivity is proportional to $p_{O_2}^{-1/6}$, and if this defect structure situation prevails over a temperature range from T_1 to T_5 , one will obtain a set of isotherms of the n-conductivity as shown in Fig.6.5.

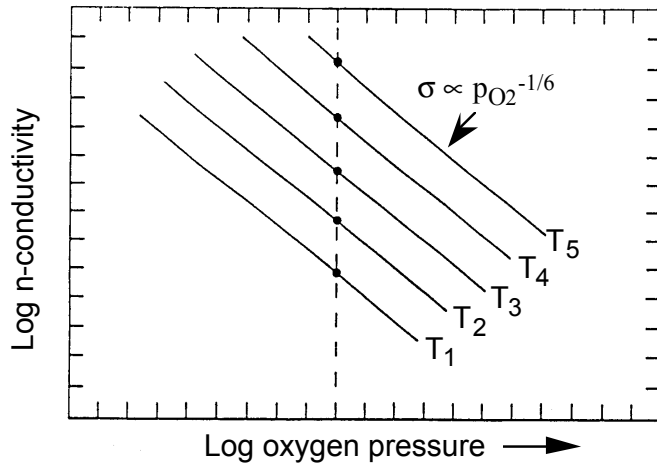


Fig.6.5 Schematic presentation of different isotherms of the n-conductivity at temperatures from T_1 to T_5 for an oxygen deficient oxide where the predominant defects are doubly charged oxygen vacancies and electrons.

Furthermore, if it can be assumed that mobility of the charge carriers (defect electrons) is independent of the defect concentration, then a plot of the values of $\log_{10}(\sigma T)$ at a constant oxygen pressure yields a straight-line relationship as illustrated in Fig.6.6. The slope of the line is given by $-\frac{1}{2.303k} \frac{\Delta H_{VO}^2}{3} + E_u$, where the factor 2.303 is the conversion factor in changing from \ln_e to \log_{10} . The activation energy is given by the term

$$E_{\sigma} = \frac{\Delta H_{VO}^2}{3} + E_u. \quad (6.62)$$

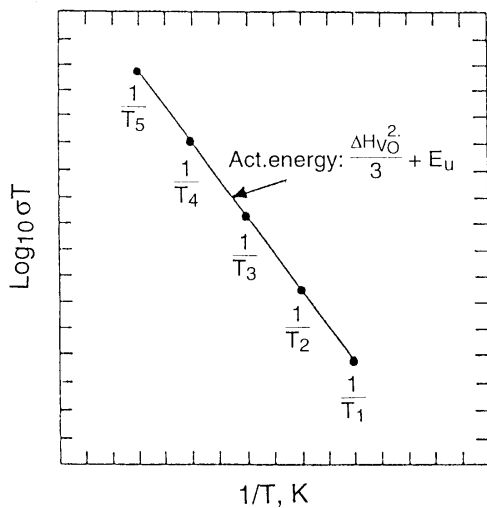


Fig.6.6 Schematic illustration of a plot of $\log_{10}(\sigma_n T)$ vs. the reciprocal absolute temperature at constant oxygen pressure (cf. Fig.6.5). The slope of the line is given by $-\frac{1}{2.303k} \frac{\Delta H_{VO}^2}{3} + E_u$ where $\frac{\Delta H_{VO}^2}{3} + E_u$ is the activation energy for the n-conductivity.

In general the temperature dependence of the charge carrier mobility of the electrons is much smaller than the enthalpy term associated with the formation of doubly charged oxygen vacancies.

The mobility of electronic charge carriers may be determined by measuring the electrical conductivity and combine these measurements with independent measurements of the concentration of the electronic charge carriers. The concentration of the charge carriers may be estimated from measurements of the Seebeck coefficient or by measurements of the nonstoichiometry combined with the proper description of the defect structure (cf. Ch.7).

For mixed conductors that exhibit both ionic and electronic conductivities it is necessary to delineate the ionic and electronic contributions. A commonly used technique for this is the emf method originally derived by Wagner. This will be described in the next chapter (Ch.7) dealing with electrochemical transport in metal oxides.

CORRELATION EFFECTS: TRACER DIFFUSION AND IONIC CONDUCTION

In the discussions of diffusion mechanisms in Chapter 5 it was pointed out that successive jumps of tracers atoms in a solid may for some mechanisms not be completely random, but are to some extent correlated. This is, for instance, the case for the vacancy and interstitialcy mechanisms. For a correlated diffusion of a tracer atom in a cubic crystal the tracer diffusion coefficient, D_t , is related to the random diffusion coefficient for the atoms, D_r , through the correlation coefficient f :

$$D_t = f D_r \quad (5.56)$$

The value of f is governed by the crystal structure and the diffusion mechanism.

Ionic conductivity method

Values of the correlation coefficient may be determined by comparing the measured values of the ionic conductivity and the tracer diffusion coefficient. Thus the use of the Nernst-Einstein relation gives the following expression for the correlation coefficient:

$$f = \frac{D_t}{D_r} = \frac{D_t c_i (z_i e)^2}{\sigma_i kT} \quad (6.63)$$

This equation is applicable to any diffusion process for which the atom jump distance is equal to the displacement of the effective charge, e.g. for vacancy and interstitial diffusion.

However, in interstitialcy diffusion the charge displacement is larger than the atom jump distance, and a displacement factor S must be included in the Nernst-Einstein relation. In

collinear interstitialcy diffusion (Fig.5.9) the effective charge is, for instance, moved a distance twice that of the tracer atom and D_t/D_r is given by

$$\frac{D_t}{D_r} = \frac{D_t c_i (z_i e)^2}{S \sigma_i kT} = \frac{f}{S} \quad (\text{collinear}) \quad (6.64)$$

where $S = 2$. For a collinear jump in an fcc structure the displacement factor is $4/3$.

Studies on alkali and silver halides have provided illustrative, and by this time, classical examples of the applicability of the ionic conductivity method for determining the correlation factor and detailed aspects of the jumps in diffusion processes. NaCl, for instance, is essentially a pure cationic conductor. Measured ratios of D_t/D_r are in good agreement with the assumption that $f = 0.78$, i.e. that the Na-ions diffuse by a vacancy mechanism.

However, such a simple relationship was not found for AgBr. AgBr is also a cationic conductor and comparative values of D_t (diffusion of Ag in AgBr) and of values of D_r evaluated from conductivity measurements are shown in Fig.6.7.

From studies of the effect of Cd-dopants on the ionic conductivity it could be concluded that cationic Frenkel defects predominate in AgBr. Thus the diffusion was therefore expected to involve both vacancy diffusion and transport of interstitial ions. The experimentally measured ratios of D_t/D_r varied from 0.46 at 150 °C to 0.67 at 350°C. For vacancy diffusion a constant ratio of 0.78 (=f) would have been expected, and the diffusion mechanism could thus be ruled out. For interstitial diffusion $f=1$, and this mechanism could also be excluded.

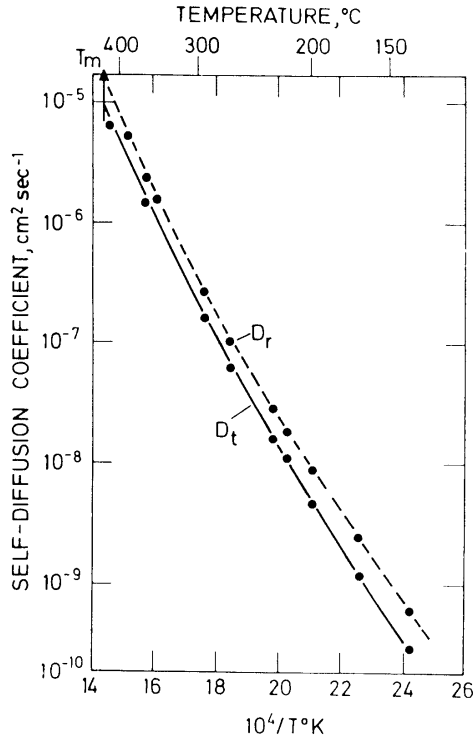


Fig.6.7. Values of D_t and of D_r evaluated from conductivity measurements for diffusion of Ag in AgBr. Results after Friauf(1957,1962).

For interstitially diffusion of Ag in AgBr the value of f equals $2/3$ for a collinear jump and 0.97 for a non-collinear jump. Following Eq.6.64 one would thus expect that D_t/D_r would range from 0.33 for a collinear jumps to 0.728 for non-collinear jumps. On this basis Friauf (1957, 1962) concluded that the interstitially diffusion is the important mechanism in AgBr and that collinear jumps are most important at low temperatures while non-collinear jumps become increasingly important the higher the temperature.

Simultaneous diffusion and electric field

The ionic conductivity and D_t may in principle be studied in a single experiment, as described by Manning (1962) and others. If a thin layer of the isotopes is sandwiched between two crystals and the diffusion anneal is performed while applying the electric field, the tracer distribution profile is displaced a distance $\Delta x = u_i Et$ relative to the profile in the absence of the applied field (Eq.5.31). The resultant tracer distribution is given by

$$c = \frac{c_o}{2(\pi D_t t)^{1/2}} \exp\left(-\frac{(x - \Delta x)^2}{4D_t t}\right) \quad (6.65)$$

The maximum in the concentration profile is - as illustrated in Fig.6.8 - displaced a distance Δx , and u_i and D_t may be determined from the same experiment. If the crystal is a mixed

ionic/electronic conductor, the value of the ionic transport number under the experimental conditions must be known.

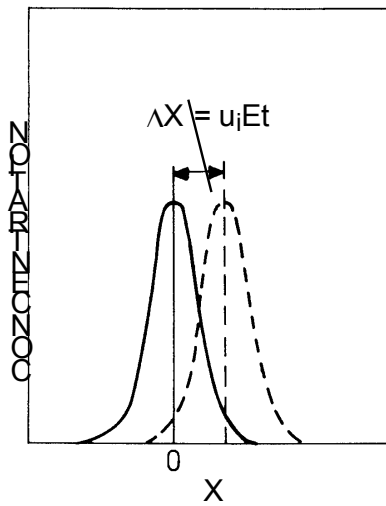


Fig.6.8 Schematic illustration of the concentration profile of a radioactive tracer when an electric field is applied during the diffusion anneal. The tracers are originally located at 0, but the concentration profile is displaced a distance $\Delta X = u_i Et$.

REFERENCES

Friauf, R.T. (1957) *Phys. Rev.* **105**, 843; (1962) *J. Appl. Phys.* **33** suppl., 494.

Manning, J.R. (1962) *J. Appl. Phys.* **33**, 2145; *Phys. Rev.* **125**, 103.