

## 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 oxide 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 (< 600-700 °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

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

where  $\phi$  is the electrical potential and  $E = -\frac{d\phi}{dx}$  is the electric field. As we have considered also in Ch. 5, the flux density of particles of type  $i$  is the product of the concentration  $c_i$  and drift velocity  $v_i$ , where the latter is given by the particle mobility  $B_i$ , and the force  $F_i$ :

$$j_i = c_i v_i = c_i B_i F_i = z_i e c_i B_i E \quad (6.2)$$

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

$$i_i = z_i e j_i = (z_i e)^2 B_i c_i E \quad (6.3)$$

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

$$u_i = z_i e B_i \quad (6.4)$$

Equation 6.3 can then be written

$$i_i = z_i e c_i u_i E = \sigma_i E \quad (6.5)$$

in which we have the very important definition of partial electrical conductivity of the species  $i$ :

$$\sigma_i = z_i e c_i u_i \quad (6.6)$$

It should be noted that Eq.6.5 is an expression of Ohm's law. The unit for the electrical conductivity is Siemens per cm,  $\text{Scm}^{-1}$  (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  $\text{cm}^3$ , and charge carrier mobility in units of  $\text{cm}^2/\text{Vs}$ . (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  $E$  always have the same sign, and  $j_i$  and  $F$  always have the same sign.  $B_i$  and  $\sigma_i$  are always positive, and it is common to neglect the sign when specifying charge mobilities  $u_i$ .

## Partial and total conductivity

The total electrical conductivity  $\sigma$  of a substance is the sum of the partial conductivities  $\sigma_i$  of the different charge carriers:

$$\sigma = \sum_i \sigma_i \quad (6.7)$$

The ratio of the partial conductivity  $\sigma_i$  to the total conductivity  $\sigma$  is termed the transport number (or transference number) of species  $i$ :

$$t_i = \frac{\sigma_i}{\sigma} \quad (6.8)$$

The native charge carriers in a binary oxide are the ions (cations and anions) and electrons. Each of these may have contributions from different transport mechanisms (defects). Most important is usually the contributions to electronic conductivity from defect (conduction band) electrons called n-type conductivity, and from electron holes, called p-type conductivity. The total conductivity is then given by

$$\sigma = \sigma_{\text{ion}} + \sigma_{\text{el}} = \sigma_c + \sigma_a + \sigma_n + \sigma_p \quad (6.9)$$

where  $\sigma_c$ ,  $\sigma_a$ ,  $\sigma_n$ , and  $\sigma_p$  are the cation, anion, electron and electron hole conductivities, respectively.

Correspondingly, the cation conductivity may have contributions from vacancy and interstitial cation conductivities, and the same applies to anions. However, we do not pursue this level of detail here.

Following Eq. 6.8 the individual conductivities may be written in terms of their transport numbers:  $\sigma_c = t_c \sigma$ ,  $\sigma_a = \sigma t_a$ ,  $\sigma_n = \sigma t_n$  and  $\sigma_p = \sigma t_p$ . Using these values Eq.6.9 takes the form

$$\sigma = \sigma (t_{\text{ion}} + t_{\text{el}}) = \sigma (t_{\text{c}} + t_{\text{a}} + t_{\text{n}} + t_{\text{p}}). \quad (6.10)$$

It may be noted that the sum of the transport numbers of all the charge carriers equals unity:

$$t_{\text{ion}} + t_{\text{el}} = t_{\text{c}} + t_{\text{a}} + t_{\text{n}} + t_{\text{p}} = 1 \quad (6.11)$$

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, as we shall see later on.

## The Nernst-Einstein relation between 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's mechanical mobility is given by

$$D_i = kTB_i \quad (6.12)$$

By combining this relation with Eqs. 6.4 and 6.5 one obtains the following relation between the random diffusion coefficient and the charge carrier mobility and the electrical conductivity:

$$D_i = kTB_i = u_i \frac{kT}{z_i e} = \sigma_i \frac{kT}{c_i z_i^2 e^2} \quad (6.13)$$

These are variants of 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, in which we will understand also when and why conduction is termed a linear process.

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  $\Delta H_m$ . When an electric field  $E$  is applied the activation energies are changed. In the forward direction of the field (downhill) the activation energy is reduced to  $\Delta H_m - \frac{1}{2} z_i e s E$  and in the reverse (uphill) direction increased to  $\Delta H_m + \frac{1}{2} z_i e s E$ . This is illustrated schematically in Figure 6-1.

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

$$j_i = \frac{1}{2} c_i s \{ \omega_{\text{forw}} - \omega_{\text{rev}} \} \quad (6.14)$$

where

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

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

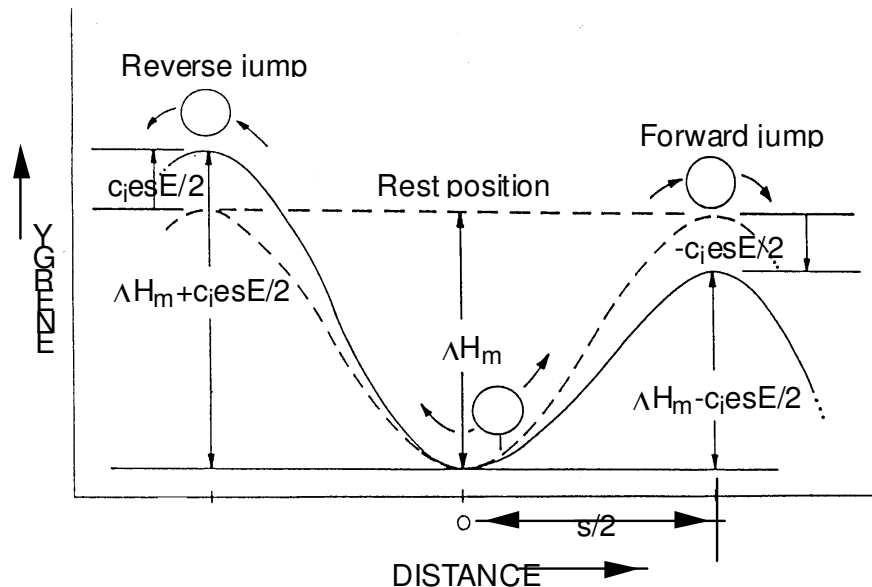


Figure 6-1. Schematic illustration of the effect of an electric field on the migration of charged species in a homogeneous crystal.  $E$  represents the electric field.  $\Delta H_m$  is the activation energy in the absence of an electric field. In the forward direction the activation energy may be considered to be lowered by  $\frac{1}{2} z_i e s E$  and increased by the same amount in the reverse direction.

Equation 6.14 then becomes

$$j_i = \frac{1}{2} c_i s \omega \left\{ \exp\left(\frac{z_i e s E}{2kT}\right) - \exp\left(-\frac{z_i e s E}{2kT}\right) \right\} \quad (6.15)$$

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 normal electrical measurements in bulk materials (and when Ohm's law is applicable), the difference in exponentials in Eq. 6.15 may be written  $z_i e s E/kT$  (since  $e^x - e^{-x} = 2x$  for  $x \ll 1$ ). Eq. 6.15 then takes the form

$$j_i = \frac{1}{2} \omega s^2 c_i \frac{z_i e E}{kT} \quad (6.16)$$

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

$$j_i = D_i \frac{c_i z_i e E}{kT} \quad (6.17)$$

We have by this shown that net flux density of a hopping charge carrier in an electrical field in the small-signal (linear) range is proportional to the random diffusion coefficient. As we have shown before, the flux of particles with a charge  $z_i e$  may also be expressed in terms of charge carrier mobility or conductivity:

$$j_i = z_i e c_i B_i E = c_i u_i E = \frac{\sigma_i E}{z_i e} \quad (6.18)$$

and when one combines Eqs. 6.17 and 6.18 one obtains various forms of the Nernst-Einstein relation (Eq. 6.13):

$$D_i = B_i kT = u_i \frac{kT}{z_i e} = \sigma_i \frac{kT}{c_i z_i^2 e^2} \quad (6.13)$$

or, rearranged,  $\sigma_i = (z_i e)^2 c_i D_i / kT$ .

It is emphasised that the relation is derived assuming random diffusion and that the mobilities and conductivity through this relation connects to the random 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, e.g. that there is no interference between ionic and electronic flows.

## Transport of electronic species

### Mobilities of electrons and electron holes

In the preceding chapters we have looked at the conductivity and charge mobility of thermally activated diffusing species and how they relate to random diffusion. In the following, we consider the charge carrier mobilities of electrons and holes.

#### *Non-polar solids – itinerant electron model*

The temperature dependence of the charge carrier mobility is dependent on the electronic structure of the solid. For a pure non-polar solid - 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 (itinerant) particles. If accelerated by an electrical field they move until they collide with a lattice imperfection. In an ideally pure and perfect crystal the mobilities of electrons and electron holes,  $u_n$  and  $u_p$ , are then 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.

$$u_{n,latt} = u_{n,latt,0} T^{-3/2} \quad u_{p,latt} = u_{p,latt,0} T^{-3/2} \quad (6.19)$$

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.

$$u_{n,imp} = u_{n,imp,0} T^{3/2} \quad u_{p,imp} = u_{p,imp,0} T^{3/2} \quad (6.20)$$

If both mechanisms are operative, each mobility is given by

$$u_n = \frac{1}{\frac{1}{u_{n,latt}} + \frac{1}{u_{n,imp}}} \quad u_p = \frac{1}{\frac{1}{u_{p,latt}} + \frac{1}{u_{p,imp}}} \quad (6.21)$$

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 (ionic) oxides*

When electrons and electron holes move through polar compounds, such as ionic 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 particle – the deformation moves along with the electron or hole.

When the interaction between the electron or electron hole and the lattice is relatively weak, the polaron is referred to as a large polaron - the deformation gives a shallow energy minimum for the location of the electron or hole. Large polarons behave much like free electronic 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

$$u_{\text{large pol.}} = u_{\text{large pol.,0}} T^{-1/2} \quad (6.22)$$

The large polaron mechanism has been suggested for highly ionic non-transition metal oxides, with large band gaps.

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.

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



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 above roughly 500 °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 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:

$$u = \frac{e}{kT} D = u_0 T^{-1} \exp\left(-\frac{E_u}{kT}\right) \quad (6.23)$$

where  $E_u$  is the activation energy for the jump.

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  $1-10 \text{ cm}^2/\text{V}\cdot\text{s}^{-1}$ , and it can be shown that a lower limit is approximately  $0.5 \text{ cm}^2/\text{V}\cdot\text{s}^{-1}$ . Small polaron mobilities generally have values in the range  $10^{-4}-10^{-2} \text{ cm}^2/\text{V}\cdot\text{s}^{-1}$ . For small polarons in the regime of activated hopping the mobility increases with increasing temperature and the upper limit is reported to be approximately  $0.1 \text{ cm}^2/\text{V}\cdot\text{s}^{-1}$ .

## Electronic conductivity

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,  $\sigma_{el}$ , is, using Eq. 6.6, given by

$$\sigma_{el} = \sigma_n + \sigma_p = enu_n + epu_p \quad (6.24)$$

where  $\sigma_n$  and  $\sigma_p$  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 charge 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 the following, we analyse the electronic conductivity in some detail for selected cases of defect structure.

#### *Intrinsic electronic semiconductor*

When the temperature of a pure, undoped semiconductor 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:

$$0 = e' + h \cdot \quad (6.25)$$

$$n \cdot p = K_i \quad (6.26)$$

where  $K_i$  is the equilibrium constant for the intrinsic ionisation, and

$$K_i = n \cdot p = N_C N_V \exp\left(-\frac{E_g}{kT}\right) \quad (6.27)$$

where  $E_g$  is the band gap,  $E_g = E_C - E_V$ , and  $N_C$  and  $N_V$  are, respectively, the densities of state in the conduction and valence bands.

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

$$n = p = K_i^{1/2} = (N_C N_V)^{1/2} \exp\left(-\frac{E_g}{2kT}\right) \quad (6.28)$$

and the electronic conductivity then becomes

$$\sigma_{el} = \sigma_n + \sigma_p = en\mu_n + ep\mu_p = e (N_C N_V)^{1/2} (u_n + u_p) \exp\left(-\frac{E_g}{2kT}\right) \quad (6.29)$$

Via differences in the mobility one of the charge carriers may dominate. 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. 6.29 is then often written

$$\sigma_{el} \approx \sigma_{el,0} \cdot \exp\left(-\frac{E_g}{2kT}\right) \quad (6.30)$$

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

#### *Effects of donors and acceptors*

A donor is a defect with an electron close to the conduction band. It is thus easily ionised to give an electron in the conduction band. Similarly, an acceptor would accept an electron from the valence band and the energy of this is close to the valence band.

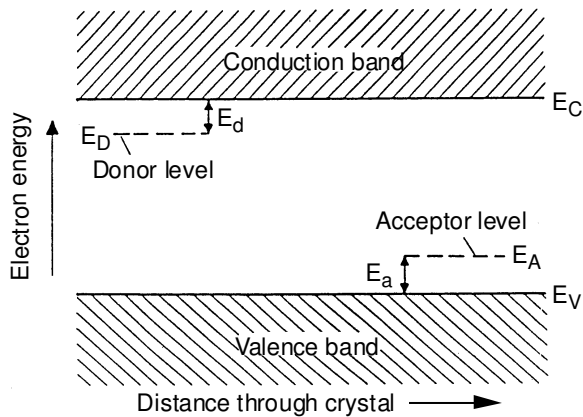


Figure 6-2. Schematic illustration of additionally localised energy levels due to donors and acceptors in the forbidden energy gap in the energy band diagram of a semiconductor.

Because of the small ionisation energies  $E_d$  and  $E_a$ , donors and acceptors are usually ionised except at very low temperatures. The compensation of the donors and acceptors may be done by electronic defects and point defects in competition with each other. In elemental and other covalent semiconductors with moderate or small band gaps, electronic defects will dominate. In these, the concentration of electronic defects compensating the donor or acceptor is thus constant. The temperature dependency of the conductivity is then only given by that of the mobility term of the charge compensating electronic defect.

In a donor-doped material with compensation by electrons, the conductivity will thus be

$$\sigma = \sigma_n = eu_n[D] \quad (6.31)$$

where the donor concentration  $[D]$  is a constant and the temperature dependency thus only given by that of the mobility  $u_n$ .

In an acceptor-doped material with compensation by electron holes, the conductivity will correspondingly be

$$\sigma = \sigma_p = eu_p[A] \quad (6.32)$$

We end this part by reminding ourselves that the temperature dependency of electronic conduction in semiconductors typically consists of two or three regions:

At the highest temperatures, intrinsic ionisation dominates and the band gap divided by two dominates the exponential temperature dependency. At intermediate temperatures the conductivity is given by a constant concentration of the electronic defect, fixed by dopants, so that only the temperature of the mobility remains. At the lowest temperatures, the dopants may not be fully ionised, and an exponential dependency of the ionisation energy of the dopant comes into play.

*Electronic conduction in nonstoichiometric oxides*

Corresponding expressions for  $\sigma_{el}$  for nonstoichiometric electronic semiconductors readily follows by considering the temperature and oxygen pressure dependence of the concentration of the electronic defects in oxides.

For nonstoichiometric oxides the concentration of electronic defects is determined by the deviation from stoichiometry, the presence of native charged point defects, and 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.

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

$$[V_O^{2\cdot}] n^2 = K_{V_O^{2\cdot}} p_{O_2}^{-1/2} \quad (6.34)$$

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

$$n = 2[V_O^{2\cdot}] \quad (6.35)$$

By combining Eqs. 6.34 and 6.35 the concentration of electrons is given by

$$n = 2[V_O^{2\cdot}] = (2K_{V_O^{2\cdot}})^{1/3} p_{O_2}^{-1/6} \quad (6.36)$$

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

$$\sigma_t = 2e[V_O^{2\cdot}]u_{V_O^{2\cdot}} + e n u_n \quad (6.37)$$

$2e[V_O^{2\cdot}]u_{V_O^{2\cdot}}$  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-type conductor where the conductivity can then be written

$$\sigma_t = \sigma_n = e n u_n = e u_n (2K_{V_O^{2\cdot}})^{1/3} p_{O_2}^{-1/6} \quad (6.38)$$

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

$$K_{V_O^{2\cdot}} = \exp\left(\frac{\Delta S_{V_O^{2\cdot}}}{k}\right) \exp\left(-\frac{\Delta H_{V_O^{2\cdot}}}{kT}\right) \quad (6.39)$$

When one combines Eqs. 6.38 and 6.39 the n-type conductivity may be written:

$$\sigma_t = \sigma_n = e u_n \exp\left(\frac{\Delta S_{V_O^{2\cdot}}}{3k}\right) \exp\left(-\frac{\Delta H_{V_O^{2\cdot}}}{3kT}\right) p_{O_2}^{-1/6} \quad (6.40)$$

Let us further assume that the electrons are small polarons and thus that the mobility of the electrons are given by Eq. 6.23. The conductivity can then be expressed by

$$\sigma_n = u_0 e \frac{1}{T} \exp\left(\frac{\Delta S_{V_O^{2\cdot}}}{3k}\right) \exp\left(-\frac{\Delta H_{V_O^{2\cdot}}/3 + E_u}{kT}\right) p_{O_2}^{-1/6} \quad (6.41)$$

Thus, following this equation the n-type 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-type conductivity as shown in Figure 6-3.

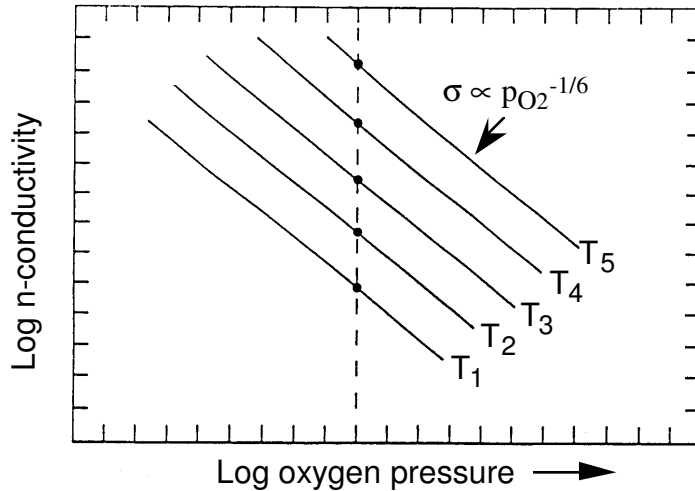


Figure 6-3. Schematic presentation of different isotherms of the  $n$ -conductivity at temperatures from  $T_1$  to  $T_5$  for an oxygen deficient oxide where the predominant defects are doubly charged oxygen vacancies and electrons.

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 Figure 6-4. 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

$$E_{\sigma} = \frac{\Delta H_{vO}^2}{3} + E_u. \quad (6.42)$$

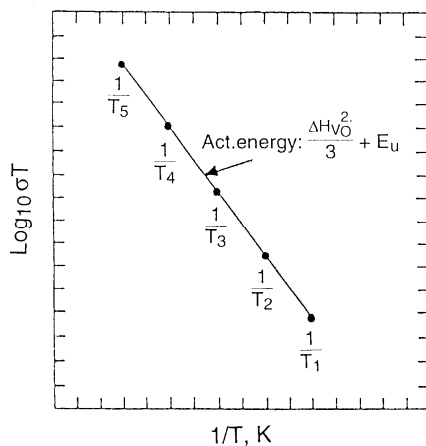


Figure 6-4. Schematic illustration of a plot of  $\log_{10}(\sigma_n T)$  vs. the reciprocal absolute temperature at constant oxygen pressure (cf. Figure 6-3).

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.

## Ionic conductivity

Ionic conductivity follows the Nernst–Einstein relationship, for hopping species, derived early in this chapter:

$$\sigma_i = z_i e c_i u_i = (z_i e)^2 c_i D_i / kT \quad (6.43)$$

It may be noted that the species considered may be a defect (e.g. oxygen vacancies) or a constituent (oxide ions). For defects the mobility and diffusivity are large and roughly constant, while the concentration is small and variable. For the constituent, the mobility and diffusivity are small and variable (with defect concentration) while the concentration is large and roughly constant. The conductivity (here oxide ion conductivity by the vacancy mechanism) is the same.

In many cases of utilizing ionic conduction, the concentration  $c_i$  of ionic defects is constant, given by a dopant. For instance, ionic conductivity in yttria-doped zirconia is determined by the concentration of oxide ion vacancies, in turn given as charge compensating the yttrium acceptors,  $2[v_{O''}] = [Y_{Zr}']$ . If the concentration of acceptors is given in mole-fraction, then it is necessary to multiply the resulting mole fraction of vacancies by the formula density or molar density of the compound in order to obtain the volume density required for insertion in Eq. 6.43:

$$\sigma_{v_{O''}} = 2e [Y_{Zr}']/2 * c_{ZrO_2} u_{v_{O''}} = 2F [Y_{Zr}']/2 * C_{ZrO_2} u_{v_{O''}} \quad (6.44)$$

where  $c_{ZrO_2}$  and  $C_{ZrO_2}$  are, respectively, the molecular and molar densities (number of formula units or moles per unit volume) of the oxide.



There are of course also cases – also of practical interest – where the concentration of ionic defects vary, e.g. with temperature in intrinsically disordered compounds, and with temperature and non-stoichiometry in non-stoichiometric compounds. In proton conducting oxides the proton conductivity varies with proton concentration, typically a function of water vapour partial pressure.

We leave further learning about ionic conduction to exercises and Chapter 7 (electrochemical transport), and here only briefly mention a couple of aspects of ionic transport that relates it in more detail to diffusion.

### 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  $f$ :

$$D_t = f D_r \quad (6.45)$$

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:

$$f = \frac{D_t}{D_r} = \frac{D_t c_i (z_i e)^2}{\sigma_i kT} \quad (6.46)$$

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 (Figure 5-10) the effective charge is, for instance, moved a distance twice that of the tracer atom and  $D_t/D_r$  is given by

$$\frac{D_t}{D_r} = \frac{D_t c_i (z_i e)^2}{S \sigma_i k T} = \frac{f}{S} \quad (\text{collinear}) \quad (6.47)$$

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 now 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 Figure 6-5.

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.

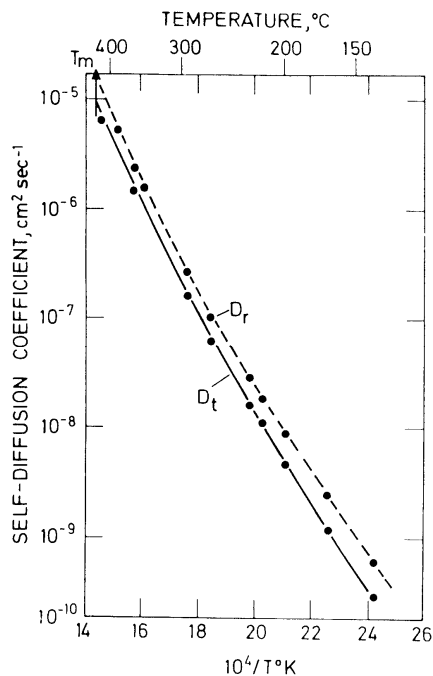


Figure 6-5. Values of  $D_t$  and of  $D_r$  evaluated from conductivity measurements for diffusion of Ag in AgBr. Results after Friauf(1957,1962).

For interstitialcy 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. 6.47 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 interstitialcy 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. The resultant tracer distribution is given by

$$c = \frac{c_o}{2(\pi D_t t)^{1/2}} \exp\left(-\frac{(x - \Delta x)^2}{4D_t t}\right) \quad (6.48)$$

The maximum in the concentration profile is - as illustrated in Figure 6-6 - displaced a distance  $\Delta x$ , 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.

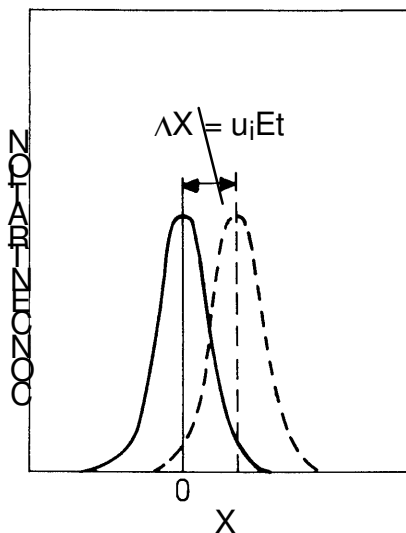


Figure 6-6. Schematic illustration of the concentration profile of a radioactive tracer when an electric field is applied during the diffusion anneal. The tracers are originally located at  $0$ , but the concentration profile is displaced a distance  $\Delta x = u_i Et$ .

## Literature

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.

## Problems

**1. Cobalt oxide:** The electronic conductivity of  $\text{Co}_{1-x}\text{O}$  at  $1350^\circ\text{C}$  and  $p_{\text{O}_2} = 0.1$  atm is 25 S/cm. Thermogravimetric measurements show that  $x = 0.008$  under the same conditions. It is assumed that singly charged cobalt vacancies are the dominating point defects. Identify the charge carriers responsible for the conductivity and calculate their charge mobility. (Assume that the density of CoO at  $1350^\circ\text{C}$  equals that at room temperature,  $6.4 \text{ g/cm}^3$ . Atomic weights  $M_{\text{Co}} = 58.93$ ,  $M_{\text{O}} = 16.00$ .)

**2. Nickel oxide:** Assume that doubly charged nickel vacancies and electron holes are the dominating defects in  $\text{Ni}_{1-x}\text{O}$  under oxidising conditions. At  $1245^\circ\text{C}$  and  $p_{\text{O}_2} = 1$  atm we know the following for the compound:

The self diffusion coefficient for nickel:  $D_{\text{Ni}} = 9 \times 10^{-11} \text{ cm}^2/\text{s}$

Electrical conductivity:<sup>7</sup>  $\sigma = 1.4 \text{ S/cm}$

Nickel vacancy concentration,<sup>8</sup> in site or mole fraction:  $[V_{\text{Ni}}''] = 2.5 \times 10^{-4}$

i) Calculate the concentration of electron holes under the given conditions, given as site fraction and as volume concentration (e.g. number/cm<sup>3</sup>). (Atomic weights  $M_{\text{Ni}} = 58.71$ ,  $M_{\text{O}} = 16.00$ , density of NiO =  $6.67 \text{ g/cm}^3$ .)

ii) Calculate the charge mobility of the electron holes.

iii) Calculate the diffusion coefficient of nickel vacancies.

iv) Calculate the charge mobility of the nickel vacancies and the ionic conductivity under the conditions referred to above.

### 3. Ca-stabilised ZrO<sub>2</sub> (CSZ)

We shall here consider a densely sintered ZrO<sub>2</sub> doped with 15 mol% CaO ( $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ ).

<sup>7</sup> Data from M.L. Volpe and J. Reddy, *J. Chem. Phys.*, **53** (1970) 1117.

<sup>8</sup> Data from W.C. Tripp and N.M. Tallan, *J. Am. Ceram. Soc.*, **53** (1970) 531.

## 6. Electrical conductivity

- i) Assume that the oxide contains doubly charged oxygen vacancies compensating the Ca dopant. What are the site-fractions of dopants and of oxygen vacancies?
- ii) Derive equations showing how the minority concentrations of defect electrons and electron holes vary with  $p_{O_2}$  in this oxide under the given conditions.
- iii) The conductivity of this oxide is independent of  $p_{O_2}$  from oxidising to very reducing conditions. What can we deduce from this?
- iv) Simpson and Carter (*J. Am. Ceram. Soc.* **49** (1966) 139) measured the self diffusion coefficient for oxygen in  $Zr_{0.85}Ca_{0.15}O_{1.85}$  and found it to be  $D_O = 2.0 \cdot 10^{-7} \text{ cm}^2/\text{s}$  at  $1100^\circ\text{C}$ . Calculate the electrical conductivity based on this.
- v) Find also the diffusion coefficient and charge mobility for the oxygen vacancies.

## 4. Intrinsic electronic conductor

- i) Equation 6.30,  $\sigma_{el} \approx \sigma_{el,0} \cdot \exp(-\frac{E_g}{2kT})$ , expresses the main feature of the temperature dependency of an intrinsic electronic conductor. Write the expression more properly, assuming that electrons have a much larger mobility than holes, that the electrons are itinerant (move in the conduction energy band) and that the material is pure and the temperature high so that lattice scattering is dominating.
- ii) You measure the conductivity and would like to find the band gap. What should you plot vs  $1/T$  to extract the band gap from the slope?

**Answers and hints to selected Problems, Ch. 6.**

to appear here...