

# Physics of Transition Metal Oxides

## Lecture 6

### Semiconducting oxides

1

### Semiconducting oxides

Remember the carrier concentration calculations in semiconductors. The conclusions were that the Fermi level would be approximately in the middle of the gap

$$E_F \approx \frac{E_c + E_v}{2},$$

and we could estimate the *intrinsic carrier concentration*

$$n = p = \sqrt{N_c N_v} \exp(-E_g/2kT).$$

These conditions rarely apply to oxides, except for very pure stoichiometric samples or very high temperatures. In most cases the carrier concentration is determined by defects or impurities.

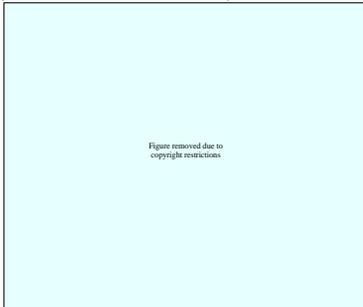
*n*-type behavior ( $n \gg p$ ) is very common, as this is caused by even a slight reduction of an insulator ( $\text{TiO}_{2-x}$ ) or by substitutional doping ( $\text{SrNb}_x\text{Ti}_{1-x}\text{O}_3$ ).

2

The charge of the extra carriers is neutralized by lattice defects, which must carry a positive net charge. It is therefore also possible to produce a bound impurity state for each electron. The energy that is needed to excite an electron from this bound state to the conduction band is the *donor ionization energy*  $E_d$ .



The typical value for  $E_d$  is 0.1 to 0.5 eV in oxides. These numbers are generally larger than for simple semiconductors, due to the larger energy gap in oxides



Grosso00 p.483

3

If we write the donor ionization process as



and remember the law of mass action

$$np \approx N_c N_v e^{\frac{-E_g}{k_B T}},$$

we can calculate the carrier concentration

$$n[D^+] = [D]N_c \exp(-E_d/kT),$$

where  $[D]$  and  $[D^+]$  are the concentrations of neutral and ionized donors. We have also replaced  $E_g$  with  $E_d$ . If these donors are the only source of carriers, we must have

$$n = [D^+].$$

and we get the carrier concentration as

$$n \propto \exp(-E_d/2kT).$$

The Fermi level is now half-way between the donor level and the conduction band bottom.

*p*-type semiconductors work the same way. Electrons can be removed by additional oxidation of a stoichiometric compound or by doping. For example,  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  is a *p*-type semiconductor.

4

The simple description only applies if there only a single type of defect present in the lattice. This is not true for oxides, in general. A *p*-type compound with metal vacancies may also have oxygen vacancies. It is thus possible to have charge *compensation*, trapping the holes produced by the majority defects.

In an *n*-type material, strong compensation by acceptor centers will give a large number of ionized donors, even if no free carriers are present and

$$n \ll [D^+]$$

This would give a donor concentration

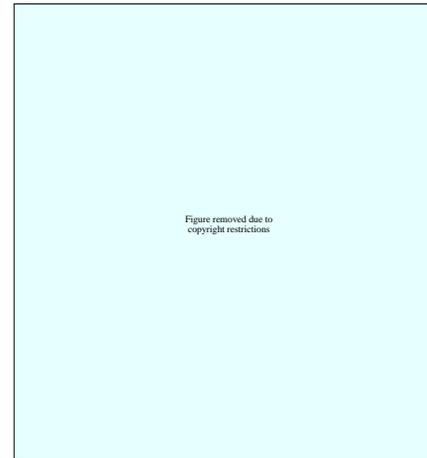
$$n \propto \exp(-E_d/kT)$$

where the activation energy is  $E_d$ , not  $E_d/2$  and the Fermi level would thus be pinned close to the donor level at an energy  $E_d$  below the conduction band edge.

The complicated structure of oxides means that strong compensation is usually present and the exact type of compensating, or even majority defects is not well known.

This discussion applied to a case where the temperature is low enough (or  $E_d$  large enough) for only a small number of donors/acceptors to be ionized.

5



The low-temperature region is known as the *freeze-out range*. At higher temperature *all* donors or acceptors are ionized and the carrier concentration does not depend on temperature. This is the *saturation range*. At very high temperatures the majority of carriers are intrinsic (i.e. thermally excited from the valence band). This is the *intrinsic range*.

Singleton01 p.61

In oxides it is often difficult to measure conductivity and thus carrier concentration or mobility. Samples are usually not single crystals, but powders or grains. Obtaining good contact between a sample and electrode is difficult. Even then, transport properties may be dominated by grain boundaries.

6

Some conductivity numbers for oxides:

Compound	Type	Mobility $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	Effective mass $m^*/m_0$	$E_a$	$E_\mu$
$\text{TiO}_{2-x}$	n	0.1	20	0.03	0
$\text{Ti}_{1-x}\text{Nb}_x\text{O}_2$	n	0.1	-	0.14	0
$\text{SrTiO}_{3-x}$	n	3	12	0	0
$\text{BaTiO}_{3-x}$	n	-	-	-	0.15
$\text{La}_{1-x}\text{Sr}_x\text{VO}_3$	p	0.15	17	0.1	0
$\text{Li}_x\text{V}_2\text{O}_5$	n	0.03	-	0.1	0.15
$\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$	p	-	-	0	0.11
$\text{Mn}_{1-x}\text{O}$	p	$10^{-5}$	-	0.5	0.4
	n	10	-	1.5	-
$\text{Li}_x\text{Mn}_{1-x}\text{O}$	p	$10^{-5}$	-	0.4	0.3
		$10^{-2}$			
$\text{Li}_x\text{Co}_{1-x}\text{O}$	p	0.4	-	0.3	0?
$\text{Li}_x\text{Ni}_{1-x}\text{O}$	p	-	6	0.3	0
$\text{LiNbO}_{3-x}$	n	-	-	-	0.4
$\text{KTaO}_{3-x}$	n	30	0.8	0	0

Cox92 p.112

7

The conductivity of an oxide is a sum over all carrier types

$$\sigma = ne\mu_e + pe\mu_h,$$

where  $\mu_e$  and  $\mu_h$  are the carrier mobilities, defined as their average drift velocity in an electric field of unit strength

In some cases, if all dominant carrier defects are fully ionized, and the number of defects is known from the chemical composition, mobility can be directly calculated from the conductivity.

The temperature dependence of conductivity often follows the *Arrhenius equation*,

$$\sigma = A \exp(-E_\sigma/kT).$$

where  $E_\sigma$  is the *activation energy* for conduction. In principle, this is the activation energy that we used in calculating the carrier concentration:

$$n \propto \exp(-E_d/2kT).$$

In practice it is not clear if we should use  $E_d$  or  $E_d/2$ , as this depends on the degree of compensation present, which is usually not known.

8

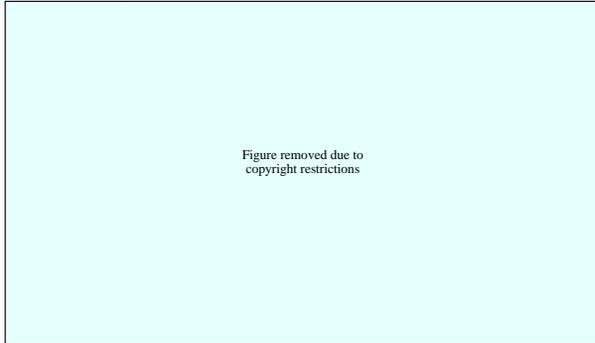
Mobility may also have a sharp temperature dependence

$$\mu = B \exp(-E_\mu/kT),$$

where  $E_\mu$  is the activation energy for hopping from site to site. In this case the total activation energy is the sum of ionization and hopping energies

$$E_\sigma = E_a + E_\mu.$$

Possible ways to determine the mobility is to measure the Hall effect or the thermopower (Seebeck effect). We start with the Seebeck effect.



9

Seebeck effect

The Seebeck effect or thermopower is used in thermocouples. What is measured is the potential difference in response to a temperature gradient. For  $n$ -type semiconductors the Seebeck coefficient is

$$\alpha = -\frac{k_B}{e} \left[ \frac{E_c - E_F}{k_B T} + A \right] = -\frac{k_B}{e} [\ln(N_c/n) + A],$$

and for  $p$ -type

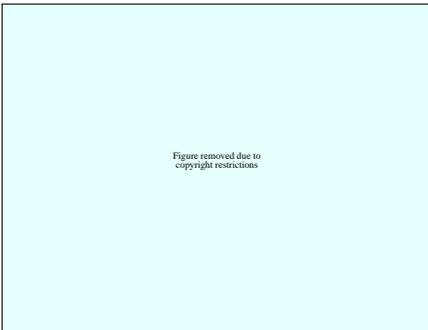
$$\alpha = +\frac{k_B}{e} \left[ \frac{E_F - E_v}{k_B T} + A \right] = +\frac{k_B}{e} [\ln(N_v/p) + A].$$

$A$  depends on how the carrier mobility varies with energy in a band. It is usually smaller than the first term and can be neglected.

The sign of  $\alpha$  will tell us what type of (dominant) charge carriers we have in a material, holes or electrons.

10

Thermopower:



Here we see the thermopower and activation energy for conduction in  $\text{Co}_{3-x}\text{Fe}_x\text{O}_4$ . At  $x = 2$  there is a switchover from  $p$  to  $n$ -type conductivity.

Cox92 p.164

The densities of available states in conduction or valence bands is given by

$$N_c(T) = 2.5 \left( \frac{m_c^*}{m} \right)^{3/2} \left( \frac{T}{300\text{K}} \right)^{3/2} \times 10^{19}/\text{cm}^3$$

$$N_v(T) = 2.5 \left( \frac{m_v^*}{m} \right)^{3/2} \left( \frac{T}{300\text{K}} \right)^{3/2} \times 10^{19}/\text{cm}^3$$

If we have an estimate for the carrier concentration (perhaps a transport measurement in a saturation temperature range, we can estimate the effective mass using a thermopower measurement.

11

For a nondegenerate semiconductor ( $E_c - E_F \gg k_B T$ ), the carrier concentration is

$$n = N_c e^{-\frac{E_c - E_F}{k_B T}}$$

If the Fermi level is pinned at the donor level,  $E_c - E_F$  is the donor ionization energy. Putting  $n$  into the thermopower expression

$$\alpha = -\frac{k_B}{e} \ln(N_c/n),$$

We can see that if we plot  $\alpha e$  as a function of  $1/T$ , we can get the activation energy for producing free carriers from the slope of the plot.



Here we have scaled thermopower and conductivity ( $\log(\sigma)$ ) of  $p$ -type NiO plotted as a function of  $1/T$ . The slopes are equal, which shows that the conduction activation energy is determined by the activation energy of ionizing a carrier. If the slopes are not the same, as in MnO, then we know that there is an additional mobility barrier in addition to the ionization barrier.

Cox92 p.165

12

In some cases, conductivity is almost completely determined by the mobility term, i.e. it is easy to produce a free carrier, but hard to hop from one site to the next site. This would happen in cases, such as  $\text{Mn}_{1-x}\text{O}$ , which contains two oxidation states,  $\text{Mn}^{2+}$  ( $d^5$ ) and  $\text{Mn}^{3+}$  ( $d^4$ ).



In this case conductivity is given by

$$\sigma = c(1-c) \frac{e^2 a^2 \nu}{k_B T} e^{-\frac{E_\mu}{k_B T}},$$

where  $c$  and  $(1-c)$  are the relative proportions of each oxidation state present in the crystal. The product,  $c(1-c)$  is the probability that a jump to a neighboring site can take place,  $a$  is the lattice constant and  $\nu$  is a hopping frequency. The exponential factor is the probability that a jump will take place. This works in e.g.  $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ , where  $\nu \approx 10^{13}$  Hz and  $E_\mu = 0.11$  eV.

13

If we only need to consider conductivity, we can also use a more simple model for thermopower (Heikes formula)

$$\alpha = \frac{k_B}{e} \left[ \ln \frac{c}{1-c} + A \right],$$

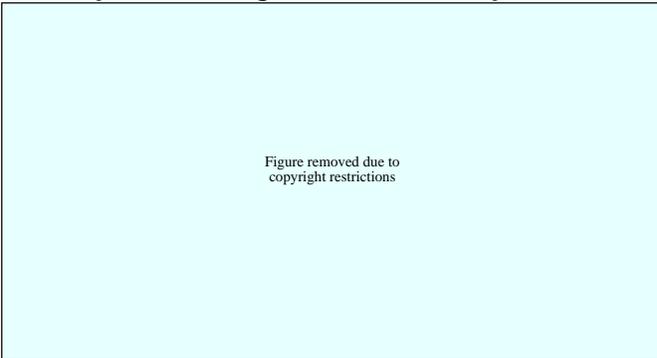
where  $c$  is the relative amount of the lower oxidation state ions ( $\text{Mn}^{2+}$ ) and  $(1-c)$  is the relative amount of the higher oxidation state ions ( $\text{Mn}^{3+}$ ). In this case the sign works out correctly, i.e. we get an  $n$ -type material when the higher oxidation state is predominant.

This formula works well for  $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ , where the calculated hole concentration  $(1-c)$  correlates well with the Sr content  $x$ .

14

## Hall effect

Another way of measuring the carrier mobility is to use the Hall effect.



Singleton01 p.134

Assume that the magnetic field is in the  $z$ -direction,  $\mathbf{B} = (0, 0, B)$ , and current flows in the  $x$  direction. Electric field is in the sample plane,  $\mathbf{E} = (E_x, E_y, 0)$ . Sample thickness is  $s$ , width is  $w$ .

15

An electron in the sample is subjected to an electric field and a magnetic field. The force on an electron is

$$\mathbf{f} = -e\mathbf{E} - e\mathbf{v} \times \mathbf{B}.$$

Current  $\mathbf{J} = -nev$  can be written in terms of electron momentum

$$\mathbf{J} = -nev = -\frac{ne}{m_e} \mathbf{p},$$

where  $m_e$  is the electron mass,  $n$  is electron density and  $\mathbf{p}$  is the average electron momentum.

In relaxation-time approximation the momentum change is

$$\frac{d\mathbf{p}(t)}{dt} = -\frac{\mathbf{p}(t)}{\tau} + \mathbf{f}(t).$$

For our Hall effect calculation this means that

$$\frac{d\mathbf{v}}{dt} = -\frac{e}{m_e} \mathbf{E} - \frac{e}{m_e} \mathbf{v} \times \mathbf{B} - \frac{\mathbf{v}}{\tau}.$$

In steady state, the derivative of  $\mathbf{v}$  is zero and thus the two components of electron velocity are

$$\begin{aligned} v_x &= -\frac{e\tau}{m_e} E_x - \omega_c \tau v_y \\ v_y &= -\frac{e\tau}{m_e} E_y + \omega_c \tau v_x \end{aligned}$$

where  $\omega_c = eB/m_e$  is the classical cyclotron resonance frequency.

16

In steady state no current flows in the  $y$ -direction and we have

$$\frac{E_y}{E_x} = -\omega_c \tau.$$

Combining this, the current density  $J_x = -en v_x$  and the expression for  $v_x$ , we have

$$R_H \equiv \frac{E_y}{J_x B} = -\frac{1}{ne},$$

where  $R_H$  is the *Hall coefficient*. This applies to electrons (simple metals).

If we have several types of carriers, as in semiconductors or oxides, we would get

$$R_H \equiv \frac{E_y}{J_x B} = \frac{1}{|e|} \frac{p\mu_{hh}^2 - n\mu_c^2}{(n\mu_c + p\mu_{hh})^2}$$

For a purely  $n$ -type semiconductor,

$$R_H = -\frac{1}{ne}$$

and for a purely  $p$ -type material

$$R_H = +\frac{1}{pe}.$$

17

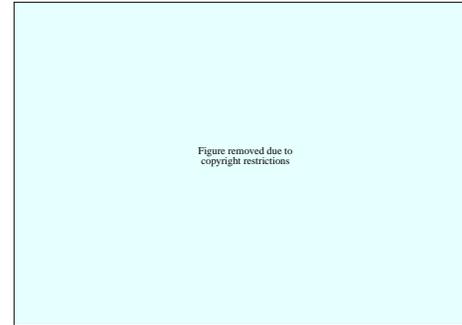
The Hall measurement thus tells us what the carrier type is ( $n$  or  $p$ ) and what the carrier concentration is. If the Hall coefficient is combined with conductivity measurement, we get the *Hall mobility*

$$\sigma R_H = -\mu_e$$

for  $n$ -type and

$$\sigma R_H = +\mu_h$$

for  $p$ -type.



Cox92 p.168

Hall mobility of reduced  $\text{TiO}_2$ . In oxides there are occasional difficulties with Hall measurements, as in  $\text{NiO}$ , where the Hall coefficient changes sign at the Neel temperature, although the material remains  $p$ -type. Hall mobility may also be different from drift mobility, seen in reduced  $\text{LiNbO}_3$ .

18

In general, mobilities are very low in oxides, which means that scattering is very rapid and the average mean-free path is comparable to the lattice spacing.

Measured mobilities can also suggest much larger effective masses than would be expected from band-structure calculations, because carriers can interact with defects and lattice vibrations.

At low temperatures the mobilities generally increase and impurity scattering dominates. At higher temperatures, interactions with lattice vibrations dominate. Theoretical models would offer a  $T^{-3/2}$  temperature dependence for mobility. Some (especially  $d^0$  compounds) deviate from this and instead show  $T^{-3}$  temperature dependence.

Magnetic oxides add additional scattering mechanisms due to the presence of ordered spins.

In oxides it is hard to guess from the composition, whether we have activated or non-activated mobility, i.e.  $\text{SrTiO}_3$ ,  $\text{LaVO}_3$ , and  $\text{NiO}$  show no activation energy, while  $\text{BaTiO}_3$ ,  $\text{LaCrO}_3$ , and  $\text{MnO}$  do have an activation energy for mobility.

19

Where does the activation energy come from?

An isolated carrier will polarize the lattice around itself. The total polarization, as discussed last time, is divided into two parts

- *electronic*: high-frequency dielectric constant, optical response
- *ionic*: low-frequency, static dielectric response.

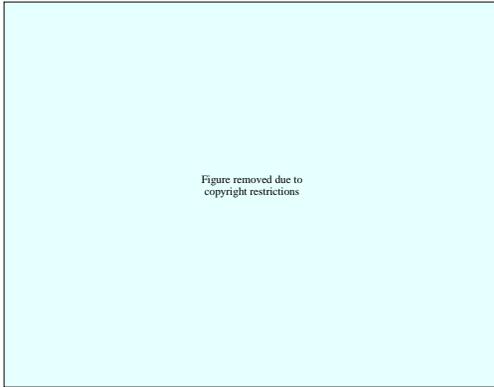
We can estimate the energy scale of polarization effects by assuming a charge in a sphere with radius  $R$  as

$$\Delta E_{\text{ion}} = -\frac{e^2}{8\pi\epsilon_0 R} \left( \frac{1}{\epsilon_{\text{opt}}} - \frac{1}{\epsilon_s} \right),$$

giving a very approximate energy scale of 1..2 eV. If the magnitude of ionic polarization is larger than  $W/2$  (half of the band width, a carrier can remain localized. This is known as a *small polaron*: trapping of a carrier at one site by the local lattice polarization which it causes.

20

Trapping thus happens when bands are narrow. This is quite typical of  $d$ -bands in transition metals. Polarons can only move from site to site by a hopping mechanism.



Cox92 p.94

This is where the mobility activation energy comes from in some oxides. If there is significant orbital overlap between neighboring sites, the barrier for hopping could be lowered (band is wider). It is possible to have a delocalized charge over two neighboring lattice sites.

21

Even when bands are wide enough for carriers to delocalize (no small polarons), it is still possible for a carrier to polarize a larger region around itself. This is known as a *large polaron*. In this case a carrier is not trapped, but the apparent effective mass will be much larger.

The mobility of small polarons increases with temperature due to faster hopping over a barrier. The mobility of large polarons decreases due to strong scattering from thermally-excited lattice vibrations.

22

### Point defects in oxides

It is easy to understand that oxygen loss in a  $d^0$  insulator, e.g.  $\text{TiO}_{2-x}$  produces extra electrons and leads to  $n$ -type behavior. In order to understand such effects better, we use a *point defect model*.

The basic types of defects are

- vacancies: an atom is missing from a lattice site
- interstitial: an extra atom occupies an irregular position
- Frenkel: vacancy plus interstitial of the same ion
- Schottky: vacancies of two different ions (in a binary)

23

### Kröger-Vink notation:

The way that we look at defects or impurities depends on what we want to understand. For spectroscopic purposes, for example, we might look at a  $\text{Cr}^{3+}$  impurity replacing  $\text{Mg}^{2+}$  in  $\text{MgO}$ ,  $\text{Al}^{3+}$  in  $\text{Al}_2\text{O}_3$ , or  $\text{Ti}^{4+}$  in  $\text{TiO}_2$  in exactly the same way.

For semiconductors there are big differences between these cases.  $\text{Cr}^{3+}$  replaces  $\text{Al}^{3+}$  without producing any extra carriers. When it replaces  $\text{Mg}^{2+}$ , we must have a compensating negative charge in the crystal. When  $\text{Ti}^{4+}$  is replaced, we need an extra hole or defect.

*Kröger-Vink notation* is used to mark the difference between the ionic charge and the charge that it replaces. Thus  $\text{Cr}^{3+}$  is neutral when replacing  $\text{Al}^{3+}$ , positive when replacing  $\text{Mg}^{2+}$  and negative when replacing  $\text{Ti}^{4+}$ .

24

Notation:

$\text{Li}_i^\bullet$	Interstitial $\text{Li}^+$ . The $\bullet$ marks a positive charge
$\text{Li}'_{\text{Mn}}$	$\text{Li}^+$ replacing $\text{Mn}^{2+}$ , giving a negative charge
$\text{Mn}^\bullet_{\text{Mn}}$	$\text{Mn}^{3+}$ replacing $\text{Mn}^{2+}$ (a hole in the Mn d-band)
$\text{Cr}^x_{\text{Al}}$	$\text{Cr}^{3+}$ replacing $\text{Al}^{3+}$ , no change of charge
$\square_{\text{O}}^{\bullet\bullet}$	$\text{O}^{2-}$ vacancy with no electron present, net +2 charge
$\square_{\text{O}}^\bullet$	$\text{O}^{2-}$ vacancy with one trapped electron also marked as $\text{F}^+$ center
$\square_{\text{O}}^x$	$\text{O}^{2-}$ vacancy with two trapped electrons (F center)

In this notation electrons would be marked  $e'$  and holes  $h^\bullet$ . These may be seen in chemical reactions involving defects, as in



which represents the insertion of lithium into an oxide, giving an interstitial  $\text{Li}^+$  and a conduction band electron.



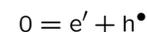
describes the compensated doping of Li into  $\text{MnO}$ , with charge being compensated by an oxygen vacancy.

25

A perfect lattice is marked with 0. The formation of a Schottky defect would be



and this shows the generation of intrinsic carriers



Defects have the role of introducing carriers into a semiconducting oxide. Defects may also provide conductivity directly, by migrating in the lattice (ionic conductivity).

Defect diffusivities are much lower than the mobility of electrons or holes. Remember that conductivity is

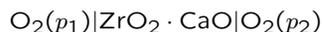
$$\sigma = \sum_i N_i e \mu_i,$$

i.e. a sum of all conduction mechanisms. Each term in the sum is a product of concentration and mobility. Electrons have much larger mobility and, if present, will dominate the transport properties.

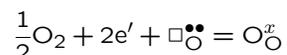
True ionic conductivity occurs in wide-gap insulators, such as  $\text{ZrO}_2$ .

26

Ionic conductivity in  $\text{ZrO}_2$  can be increased by doping with  $\text{CaO}$  or  $\text{Y}_2\text{O}_3$ . These are used as solid electrolytes in oxygen sensors



Both sides are coated with a platinum catalyst and we get a reaction



Oxide ions can diffuse through the zirconia membrane. Such a cell produces a potential

$$E = k_B T / 4e \ln(p_2/p_1)$$

Such sensors are widely used in cars to monitor engine performance.

27

Defect spectroscopy

The precise nature of defects in oxides is hard to analyze, since direct defect structure observation is not usually possible. Spectroscopic techniques are often used.

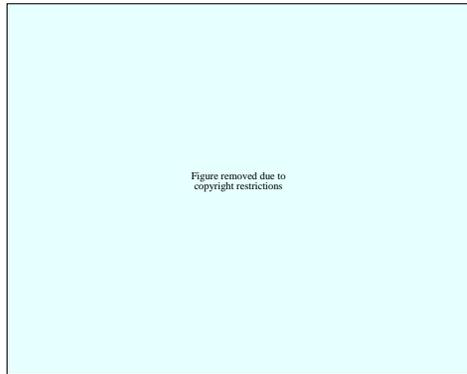
Introduction of carriers usually gives rise to strong absorption bands. These bands are usually very broad and extend into the visible range. Doped insulators thus usually have some color. Heavily-doped crystals become black.

There are various light absorption mechanisms. We already looked at direct band-to-band transitions (gap energy).

*Free-carrier absorption* involves carriers within a band. Absorption is mediated by some form of scattering process. This would happen in heavily-doped oxides with large numbers of ionized carriers that do not form small polarons. Absorption should fall with increasing wavelength as  $\lambda^n$ , where  $n=2$  for acoustic-mode scattering, 2.5 for optic-mode scattering, and 3 for ionized-impurity scattering.

28

## Optical absorption



This mechanism is common in lightly reduced  $\text{WO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{KTaO}_3$ . This plot shows bipolaron absorption in  $\text{WO}_3$  (a) and defect absorption after illumination (b).

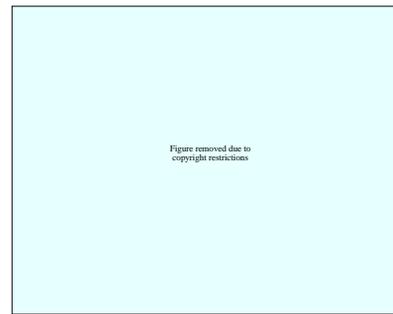
The power law dependence is only approximate, so determining scattering mechanisms from this data is not possible. The exponent is usually in the range 2...3.

Cox92 p.188

In  $\text{SrTiO}_3$ , for example, several mechanisms contribute, including charged oxygen vacancies  $\square_{\text{O}}^{\bullet}$ . The absorption in  $\text{WO}_3$  is attributed to polarons, accompanied by carrier localization and strong localized lattice distortions. What is odd in  $\text{WO}_3$  is that the material does not show an ESR signal in the dark condition (no unpaired electrons). What appears to happen is that carriers are trapped in pairs at neighboring  $\text{W}^{5+}$  sites. These are known as bipolarons.

29

## Absorption energy



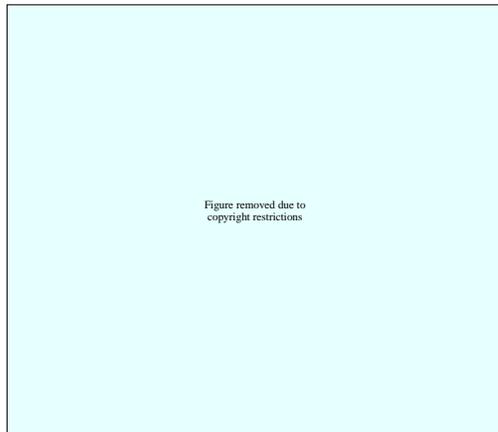
The polaron discussion showed that the optical absorption energy should be related to the mobility activation energy.

In a simple parabolic case

$$E_{\text{opt}} = 4E_{\mu}.$$

Optical absorption of defect states is often difficult due to the intense absorption. One way is to use very low defect concentrations. Other way is to use a different probing technique, such as electron energy loss spectroscopy (EELS), photoelectron spectroscopy (PES), or dielectric loss measurements.

30



These figures show how the EELS spectrum changes with doping in  $\text{Na}_x\text{WO}_3$  in (a) and photoelectron spectra are shown in (b).

Above  $x = 0.3$  this material is metallic. We look what happens below  $x = 0.3$ . EELS shows a broad loss peak with a maximum at around 1 eV. This is similar to the optical absorption.

The PES result shows a peak that does not change in shape below  $x = 0.3$ . Only the intensity drops as the number of defects drops. The peak width is controlled by vibrational excitations at the  $\text{W}^{5+}$  localization site of a polaron.

Cox92 p.188

31

## Carrier activity

In order to get a conducting crystal by doping, we need to ionize the carriers. If we think of a localized carrier at a defect site, the 'hydrogen' model would give an ionization energy of

$$E_c = R(m^*/m_0)/\epsilon_r^2,$$

where  $R$  is the Rydberg constant, 13.6 eV,  $m^*$  is the effective mass of a carrier, and  $\epsilon_r$  is the relative dielectric constant of the material.

Several problems here:

- What effective mass to use?
- How does the band structure affect the effective mass?
- Which  $\epsilon$  to use? (static or optical)

32

If the effective mass of a carrier is enhanced by polaron formation, the static (low-frequency, slow) dielectric constant should be used.

At the same time, the hydrogen model only applies when the impurity orbital radius  $a_0$

$$a_0 = a_H \epsilon_r / (m^* / m_0)$$

is much larger than the lattice spacing.  $a_H = 53$  pm, is the hydrogenic Bohr radius. If  $(m^* / m) = 10$ , this requires a dielectric constant of over 100. This is true in SrTiO<sub>3</sub> and KTaO<sub>3</sub>. In SrTiO<sub>3</sub>,  $(m^* / m_0) = 12m_0$  and  $\epsilon_r \approx 220$  at room temperature. This would give a binding energy of about 3 meV and less than 0.1 meV for KTaO<sub>3</sub>.

This shows why SrTiO<sub>3</sub> becomes metallic at a rather low doping level of about 0.5% because the impurity orbitals start to overlap.

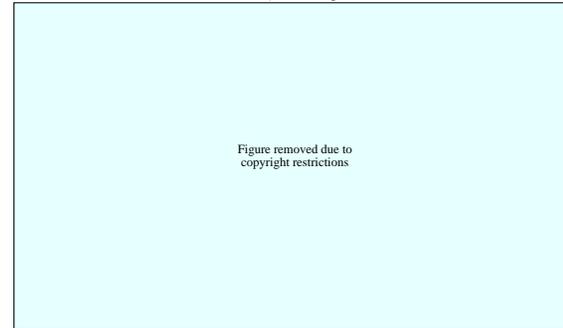
In other oxides, where  $\epsilon$  is much smaller, the radius is also smaller, comparable to the metal-metal distance. Localization of a carrier in a small volume like this will create strong polarization effects which must be included in any ionization energy calculation. A hydrogen model would not be accurate.

Ionic model would be more accurate here, but it only handles holes in metal orbitals. Photoelectron measurements clearly show that holes are often at the oxygen site, instead of the metal. So an ionic model would also fail.

33

Semiconductor-to-metal transitions:

Semiconductors become completely metallic when heavily doped.

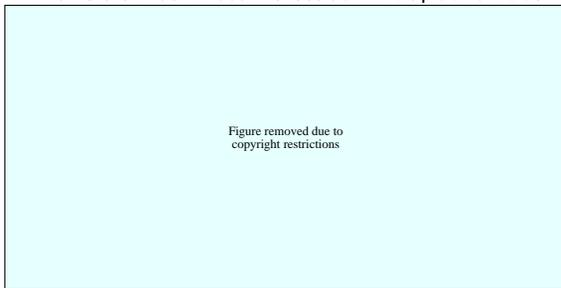


Cox92 p.193

Here we look what happens to heavily doped SrVO<sub>3</sub>, i.e. La<sub>1-x</sub>Sr<sub>x</sub>VO<sub>3</sub> as a function of doping level  $x$ . As we see, the activation energy drops as the doping level increases. At  $x = 0.2$  the activation energy becomes zero and we get a metal.

34

Transition to metallic state in doped oxides



Even when there is no transition, as in Li-doped NiO, the activation energy still drops with doping. This could be due to increased dielectric constant due to the extra polarizability of the impurity states. Higher  $\epsilon$  weakens carrier binding to the impurities.

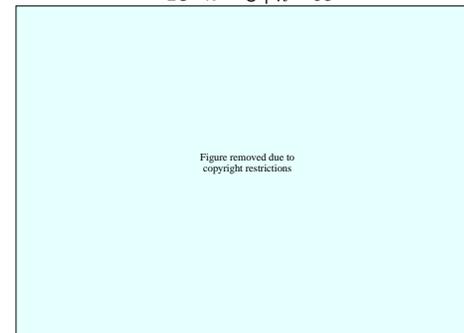
In various heavily-doped oxides, the Arrhenius activation energy plot does not work. It is more accurate to use

$$\sigma = Ae^{-\left(\frac{T_0}{T}\right)^{1/4}},$$

where  $A$  and  $T_0$  are constants.

35

This can be seen in Nb<sub>18-n</sub>W<sub>8+n</sub>O<sub>69</sub>



Cox92 p.194

The carrier concentration goes up with  $n$ . At highest  $n$  there is no temperature dependence, i.e. we have a metallic state. The  $T^{1/4}$  exponent is a sign of a *variable range hopping* mechanism of conduction.

36

**References:**

Grosso00 G. Grosso, G. P. Parravicini, "Solid State Physics", Academic Press, San Diego, 2000.

Singleton01 J. Singleton, "Band Theory and Electronic Properties of Solids", Oxford University Press, Oxford, 2001.

Cox92 P. A. Cox, "Transition Metal Oxides: An Introduction to Their Electronic Structure and Properties", Clarendon press, Oxford, 1992.