Physics of Transition Metal Oxides

Lecture 7

Metallic oxides

Activation energy of conduction

In a system where carriers are more or less localized at defect sites, we would expect to see an activation energy, i.e. an energy barrier that a crrier has to cross to become mobile (ionization energy). Mobile carriers have to cross a barrier when jumping from one lattice site to another (mobility barrier). Conductivity follows the *Arrhenius equation*

$$\sigma = A\mathrm{e}^{-\frac{E_\sigma}{k_B T}}.$$

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The activation energy $E_\sigma = E_\mu + E_a$, where E_μ is the mobility activation energy and E_a is the carrier ionization energy barrier.

This plot shows how a carbon resistor (Allen-Bradley 270Ω) behaves.

Singleton01 p.129

We now move from seiconductors to metallic systems. In a metal we would not have an activation energy for carrier movement. We look at how the activation energies are affected by the concentration of dopants in a crystal.

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Here we have a plot showing the conductivity of Ge doped with Sb. The doping level is 10^{15} cm^{-3} (donors). The sample is partially compensated with $\approx 10^{13}$ cm^{-3} of acceptors.

At high temperature all carriers are ionized and the temperature dependence is due to a change in mobility (phonon scattering, $\mu \propto T^{-3/2}$). For Ge this happens above 30 K.

McClintock84 p.81

In this plot, we see two slopes with a jump at 4 K. In this temperature range the main resistivity change is due to the ionization of carriers. The jump at 4 K is due to the presence of a small amount of compensating acceptor states.

At very low temperatures, we start to see a quantum-mechanical tunneling or *hopping* mechanism. A classical electron would be trapped on a particular site at $\mathbf{r}_1$ in a crystal. A potential barrier separates it from other sites. The quantum-mechanical wavefunction of the electron extends much further and there is a finite probability of jumping (tunneling) to another site.

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The probability of jumping, P_{12}, depends on how far the next impurity site is

$$P_{12} \propto \mathrm{e}^{-2\frac{|\mathbf{r}_1-\mathbf{r}_2|}{a_0}}$$

The probability also depends on the energy difference at the two sites $(E_1 - E_2)$. This difference has to come from phonons.

$$P_{12} \propto \mathrm{e}^{-2\frac{|\mathbf{r}_1-\mathbf{r}_2|}{a_0}-\frac{E_1-E_2}{k_B T}}$$

The electrical conductivity is proportional to P_{12}. This is a nearest neighbor hopping mechanism and it predicts an exponential temperature dependence for resistivity at low temperatures. It is only possible if $E_1 - E_2 \ll k_B T$.

Semiconductor-to-metal transitions:

Semiconductors become completely metallic when heavily doped.

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Here we look what happens to heavily doped SrVO$_3$, i.e. La$_{1-x}$Sr$_x$VO$_3$ 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.

Transition to metallic state in doped oxides

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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 ϵ weakens carrier binding to the impurities.

In various heavily-doped oxides, the Arrhenius activation energy plot does not work. In this case the distance between impurity sites is small and the electron energy difference at two different sites is more important. Effectively an electron can hop a longer distance if the energy difference $E_1 - E_2$ is negative for the same value of P_{12}. This is *variable range hopping* and it is more accurate to use

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

where A and T_0 are constants.

This can be seen in Nb$_{18-n}$W$_{8+n}$O$_{69}$

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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.

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Variable range hopping is a general feature of disordered systems. Impurities in an oxide lattice is one case. More generally this is seen in amorphous materials.

McClintock84 p.84

Transitions to the metallic state can be seen in various measurements. The Seebeck coefficients of metals are generally lower than those of semiconductors. A drop of thermopower usually happens close to the transition.
In other spectroscopic measurements a Fermi level crossing appears in photoelectron measurements, a plasma peak appears in EELS, etc.

The transition is also visible by eye in oxide bronzes, such as Na$_x$WO$_3$ (generally doped d^0 oxides). At low x the color is blue (absorption in infrared). At higher x the color changes to red and then bronze as the metallic state is reached.

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As a practical example, here we have the resistance behavior of a Ruthenium oxide resistor. The oxide contains a large number of disordered defects.

As a general rule, a transition to metallic state occurs when the carrier concentration is in the range of 0.2 to 0.3 carriers per transition metal atom. At the transition the conductivity is $10^2 - 10^3 (\Omega\,\mathrm{cm})^{-1}$. Exceptions are SrTiO$_3$ and KTaO$_3$ due to their high dielectric constants.

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Let's look at the semiconductor-to-metal transition in a density of states picture.

When the doping level is low (a), we get a sharp impurity (this figure is for a donor) peak in the gap.

If the concentration of impurities increases, the carriers trapped at these site start to overlap, forming a narrow impurity band (b). Since each defect donates a single electron, this band should be exactly half-filled.

Localized electrons also suffer from strong electron-electron interactions, resulting in a Hubbard split of the impurity band. The Hubbard U in this case is the Coulomb repulsion between two electrons in the same defect orbital. Typically the Hubbard gap is comparable to E_d and the upper Hubbard impurity band thus partly overlaps with the bottom of the conduction band. (c)

At even higher concentrations (d), the impurity bands broaden and overlap. Conductivity does not appear due to *Anderson localization*.

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If we look at *disordered* impurities in a crystal, each with a slightly different energy, they form a narrow band. The impurities that are in the middle of the band (there are many of those) are likely to have a neighbor with a similar energy. In that case overlap can happen and carriers can move. The impurities with an energy close to a band edge are very unlikely to have a neighbor with a similar energy. Carriers at those sites belong to the 'band' but they are completely localized and can not contribute to metallic conduction.

We can thus have case where the Fermi level is inside a band, but not get metallic conductivity. The localized/mobile boundary is sharp, and is known as a *mobility edge*. The localized carriers can only move by hopping.

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That is why case (d) does not give a metal and we can expect a $T^{1/4}$ temperature behavior close to the transition to metallic state.

At the highest doping levels, the bands are so broad that delocalization occurs at the Fermi level and we get a metal (e).

The various steps listed here are not of equal importance. For example, the Nb-W oxide system shows a variable range hopping behavior over a broad composition range.

In partly compensated semiconductors the Fermi level may shift into the lower Hubbard band. In this case we may be looking at the mobility edge within this band instead (compensation matters).

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The conductivity change can be very sharp close to the transition, as shown here for phosphorous-doped Si. Mott predicted that the transition would occur universally at

$$n_c^{1/3} a_0 = 0.26 \pm 0.05,$$

where n_c is the critical carrier concentration and a_0 is the radius of the impurity orbital. In oxides this model works well in high dielectric constant oxides like $SrTiO_3$ or $KTaO_3$ because the impurity orbital size is given by

$$a_0 = a_{\mathrm{H}} \frac{\epsilon_r}{m^*/m_0}$$

and thus the orbitals in those materials are large and the hydrogen model works well.

McClintock84 p.85

For $SrTiO_3$ we have (at RT) $m^* = 12$ and $\epsilon_r = 220$, giving $a_0 = 1$ nm. The estimated $n_c \sim 5 \times 10^{18}$ cm^{-3}. Measured value is about 3×10^{18}.

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This plot shows just how well the Mott prediction works in various materials.

Mott also analyzed the transition, starting from the metallic side. A metal should lose conductivity when the scattering due to disorder reduces the mean-free path to a value which is comparable to the lattice constant. Mott thus predicted a minimum metallic conductivity of

$$\sigma_{\mathrm{min}} = 0.026 \frac{e^2}{\hbar a}.$$

For $a = 0.3$ nm, this gives 300 $(\Omega\ \mathrm{cm})^{-1}$. The experimental numerical values are around 1000 $(\Omega\ \mathrm{cm})^{-1}$.

McClintock84 p.86

Metallic oxides:

Metals are characterized by a resistivity that increases with temperature. *Simple metals* are materials where the free-electron theory gives a good description of the band structure and transport properties.

There are very few simple metals among oxides (ReO_3, Na_xWO_3). This is due to electrn-electron interactions or *correlations* that are inevitable when bands are narrow (as d-bands are). Carriers may also interact with the lattice. This occasionally induces a transition to an insulating state at low temperature or a transition to a superconducting state.

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Here we have the band diagram of ReO_3

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A simple cubic lattice with a single formula unit per unit cell.

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The valence band consists mostly of O $2s$ and $2p$ levels. Slight admixture of Re $5d$ as well.

The conduction band is mostly Re $5d$. The Re $5d$ band has crystal-field splitting into a t_{2g} band and an e_g band.

The band width is determined by the mixing of Re $5d$ and O $2p$ levels, not by Re orbital overlap.

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The orbital orientation is such that there is practically no mixing of O $2p$ and Re $5d$ orbitals at the Γ point.

Rao98 p.258

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Three d levels are degenerate at the Γ point. Bonding depends on the direction of $\mathbf{k}$, which is why the three bands split in some of the other regions in k-space. One branch is nearly flat in the ΓX direction.

The shape of the Fermi surface of metallic oxides can be measured in some cases, such as ReO_3 because the mean-free path of electrons is long enough (resistivity is $10^7 (\Omega\,\mathrm{cm})^{-1}$ at low temperature. The calculated shape can be checked by measuring the de Haas-van Alphen effect (oscillation of sample magnetization in a strong magnetic field). In most other oxides, even conducting, the mean-free path is comparable to a lattice constant.

The band structure of Na_xWO_3 with $x > 0.4$ is similar to ReO_3. The sodium occupies randomly some of the large interstitial sites in the lattice. The conduction band is also due to W-O hybridized bands. The Na orbitals have much higher energy.

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The density of states at E_F has been measured using photoelectron spectroscopy (□) and specific heat (●). The dashed line shows a free-electron model calculation with $m^* = m_0$.

Specific heat is

$$C = \alpha T^3 + \gamma T,$$

where the T^3 term comes from phonons and the multiplier γ of the linear term is proportional to $N(E_F)$

$$C_{\mathrm{el}} = (\pi^2/3) k_B^2 T N(E_F).$$

The measurements confirm that each sodium gives a single carrier.

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The measured results give a linear $N(E_F)$, while the free-electron prediction is

$$N(E_F) \propto m^* x^{1/3}.$$

This illustrates some of the difficulties in analyzing oxide data. What is not clear for the tungsten bronzes is whether the electronic structure can be analyzed by a rigid-band model. In this case the doping would only shift the Fermi level without actually changing the shape of the bands. In Na_xWO_3 we would need to consider

- The disordered occupancy of interstitial sites by Na^+ ions
- Polaron formation
- Coulomb interactions

All these influences may be present in the metallic regime as well, distorting the density of states. There is also a slight increase in the W-W distance as doping level increases (due to the introduction of electrons into antibonding orbitals). This would decrease orbital overlap and make the bands narrower (effective masses larger). The linear $N(E_F)$ dependence is probably a sum of many influences.

Transport properties

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Cox92 p.211

ReO_3 has an exceptionally high conductivity (for an oxide) of $10^7 (\Omega\,\mathrm{cm})^{-1}$. At room temperature it is still 10 times more conducting than the best tungsten bronzes. The disorder caused by Na doping clearly has an effect.

The resistivity behavior shown here is for Na_xWO_3. The resistivity can be separated into two terms

$$1/\sigma = \rho = \rho_{\mathrm{dis}} + \rho_{\mathrm{lat}},$$

where ρ_{dis} is the residual resistivity at low temperature due to scattering by static disorder and ρ_{lat} is the contribution of lattice vibrations.

The diorder scattering term is very large at 4 K. For $x = 0.5$ it contributes about one half of the room-temperature resistivity. Disorder is reduced as the Na sites are filled up with x increasing from 0.5 to 0.9. This results in a 10-fold drop of resistivity. The bump at $x = 0.75$ is due to partial Na ordering as shown by neutron diffraction.

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For a free-electron system we would have a Hall coefficient

$$R_{\mathrm{H}} = -\frac{1}{ne}$$

The measured results shows a close to linear dpendence, but slightly higher than what would be calculated from the composition of the sample. This deviation is due to the deviation of the electronic structure from a pure free-electron case.

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The measured Seebeck effect gives approximately linear temperature dependencies, as expected for a metal

$$\alpha_d = (\pi^2/3)(k^2/e)T/E_F$$

As the doping level inreases the Fermi level shifts and also changes the thermopower. The Fermi level shifts calculated from the Seebeck measurements don't quite fit free-electron predictions either.

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Optical properties

A good metal should behave like a plasma, i.e. a neutral gas of light electrons and heavy ions. A free electron in such a model would feel an external oscillating electric field (a light wave) and the equation of motion for an electron would be

$$m_0 \frac{d^2x}{dt^2} + m_0\gamma\frac{dx}{dt} = -e\mathcal{E}(t) = -e\mathcal{E}_0 \mathrm{e}^{-i\omega t}.$$

The first term is the acceleration of the electron, the second term is a frictional damping force of the medium. Obviously, the electron also oscillates, and we can substitute for the electron $x = x_0\mathrm{e}^{-i\omega t}$

$$x(t) = \frac{e\mathcal{E}(t)}{m_0(\omega^2 + i\gamma\omega)}.$$

The polarization of the gas is $-Nex$, where N is the volume density of electrons. The electric displacement is thus

$$\begin{aligned} D &= \epsilon_r\epsilon_0\mathcal{E} \\ &= \epsilon_0\mathcal{E} + P \\ &= \epsilon_0\mathcal{E} - \frac{Ne^2\mathcal{E}}{m_0(\omega^2 + i\gamma\omega)} \end{aligned}$$

This gives us the relative dielectric constant

$$\epsilon_r(\omega) = 1 - \frac{Ne^2}{\epsilon_0 m_0}\frac{1}{(\omega^2 + i\gamma\omega)} = 1 - \frac{\omega_p^2}{(\omega^2 + i\gamma\omega)},$$

where

$$\omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 m_0}}$$

is the *plasma frequency*.

When damping (scattering) is small, we have $\gamma = 0$ and

$$\epsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2}.$$

The complex refractive index $\tilde{n} = \sqrt{\epsilon_r}$ and thus $\tilde{n}$ is imaginary when $\omega < \omega_p$ and zero when $\omega = \omega_p$. Reflectivity is given by

$$R = \left|\frac{\tilde{n} - 1}{\tilde{n} + 1}\right|^2.$$

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Substituting $\tilde{n}$ into this shows that reflectivity is unity for $\omega \leq \omega_p$ and decreases for $\omega > \omega_p$. For metals the plasma frequency is typically in the ultraviolet region.

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This is the reflectivity of silver, showing why metals make good mirrors. The color of some metals, like copper, are due to interband transitions, not due to free-electron reflectivity changes.

Fox01 p.12,145

In oxides (and semiconductors in general) we have a slightly more complicated behavior because there are other sources of polarization in addition to free electrons.

$$\begin{aligned} D &= \epsilon_r \epsilon_0 \mathcal{E} \\ &= \epsilon_0 \mathcal{E} + P_{\text{other}} + P_{\text{freecarrier}} \\ &= \epsilon_{\text{opt}} \epsilon_0 \mathcal{E} - \frac{Ne^2 \mathcal{E}}{m^*(\omega^2 + i\gamma\omega)} \end{aligned}$$

Herte P_{other} is due to bound electrons, while m^* accounts for the band structure and N is the carrier concentration. In this case we get

$$\omega_p^2 = \frac{Ne^2}{\epsilon_{\text{opt}} \epsilon_0 m^*},$$

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where ϵ_{opt} is the optical dielectric constant obtained from $\epsilon_{\text{opt}} = n^2$, measured well below the interband absorption edge, where a semiconductor would be completely transparent. For typical semiconductors this edge is in the infrared region.

Fox01 p.156

In oxides, the plasma edge can be in the visible range

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This example is for ReO_3. The spectrum shape is complicated by various intra- and interband transitions.

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The band structure of ReO_3 is not quite free-electron like and we see quite large oscillations of the dielectric constant above the plasma frequency due to interband transitions. The dip just below the edge occurs at

$$\omega^2 = \frac{\epsilon_{\text{opt}}}{\epsilon_{\text{opt}} - 1} \omega_p^2$$

can be used to find an *optical effective mass* of $0.86 m_0$ for the $\omega_p = 2.3$ eV of ReO_3.

Cox92 p.213

The lowest energy interband transition is at 4.2 eV and is due to valence band-conduction band transitions (similar to a band-gap transition of d^0 oxides). The energy is larger than the gap because the bottom of the conduction band is already full.

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The plasma frequency can also be measured by EELS, i.e. measuring the loss of energy when electrons are reflected from the surface, assuming that the surface properties are characteristic of the bulk. In this case

$$\omega_{\text{sp}}^2 = \frac{ne^2}{\epsilon_0 (\epsilon_{\text{opt}} + 1) m^*}$$

The measure m^* values for Na_xWO_3 are shown here (●). These coincide with the optical plasma edge measurements (△), but not with photoelectron spectroscopy results (○).

This difference is not really surprising, considering all the other data, which shows that although the oxides are metallic, they are far from a free-electron system.

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A direct way to measure $N(E_F)$ is photoelectron spectroscopy. A few cautionary words here about this technique. The plot shows an XPS spectrum of ReO_3 and the total density of states. The relative occupancies of the conduction band and valence band are quite different in the two plots. This is due to a different ionization cross-section for electrons in different orbitals.

Cox92 p.215

In this case the cross-section of Re $5d$ orbitals is much larger than for the O $2p$ orbitals and therefore the spectrum is a good approximation of the Re $5d$ partial density of states, not really the total density of states.

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