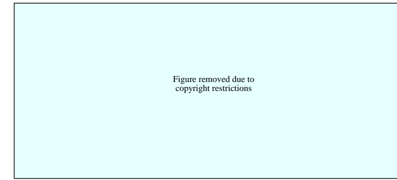
Physics of Transition Metal Oxides

Lecture 4

Insulating oxides

We focus on insulators, but first, we have to understand what we mean by the word *insulator*.



Ashcroft76 p.562

If the band structure of a material has a gap and the Fermi level is within this gap (a band is exactly full), we would have an insulator or a semiconductor. If there is no gap, we would have a metal.

The boundary between an insulator and a semiconductor is not as clear.

At absolute zero, the highest completely filled band (the *valence band*) is separated from the lowest empty band (the *conduction band*) by a gap E_g. At $T = 0$ the material can not conduct electricity. If $T > 0$, various mechanisms can cause electrons to be excited into the conduction band.

We start with conductivity of metals

Remember the band structure calculation. This told us that

$$E(\mathbf{k}) = E_0 - 2t_x \cos(k_x a) - 2t_y \cos(k_y b) - 2t_z \cos(k_z c),$$

or (for simplicity) in one dimension

$$E(k) = E_0 - 2I \cos(k\, a).$$

We also derived values for electron velocity and effective mass

$$v \equiv \frac{1}{\hbar}\frac{\mathrm{d}E}{\mathrm{d}k} = \frac{2Ia}{\hbar}\sin(k\, a),$$

$$m^* \equiv \frac{\hbar^2}{\frac{\mathrm{d}^2E}{\mathrm{d}k^2}} = \frac{\hbar^2}{2Ia^2}\frac{1}{\cos(ka)}.$$

We also calculated a classical response to an external field for a conduction electron

$$\hbar\frac{\mathrm{d}k}{\mathrm{d}t} \equiv f.$$

Let's assume we have an electron at the conduction band bottom, with $k = 0$ for $t < 0$. At $t = 0$ an electric field ϵ is switched on in the x direction. For $t \geq 0$ the force on the electron is $f = -e\epsilon$ and thus

$$\hbar\frac{\mathrm{d}k}{\mathrm{d}t} = -e\epsilon.$$

Integrate this with boundary condition $k = 0$ at $t = 0$

$$k(t) = -\frac{e\epsilon}{\hbar}t.$$

and substitute into the equations for v and m^*

$$v = -\frac{2Ia}{\hbar}\sin(\frac{a\epsilon e t}{\hbar})$$

and

$$m^* = \frac{\hbar^2}{2Ia^2}\frac{1}{\cos(\frac{a\epsilon e t}{\hbar})}.$$

We can now integrate v to get the position of an electron, x

$$x = \frac{2I}{e\epsilon}\left[\cos(\frac{a\epsilon e t}{\hbar}) - 1\right].$$

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The electron position and velocity oscillate around a fixed value (*Bloch oscillations*) at an angular frequency of $\omega_B = a\epsilon e/\hbar$! This means that there can be no current flow and a material with free electrons should be an insulator.
For a field of $\epsilon = 10^4$ V/cm, we get

$$\omega_B = \begin{cases} 1.5192 \times 10^{11} \text{rad/sec} & \text{for} a = 1\text{Å} \\ 1.5192 \times 10^{13} \text{rad/sec} & \text{for} a = 100\text{Å}. \end{cases}$$

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Why this happens? As an electron accelerates, it moves up the $E(k)$ curve until it reaches the top of a band at $k = -\pi/a$. At that point the band is flat, and the derivative of $E(k)$ is also zero, i.e. $v \to 0$ and $m^* \to \infty$.
If there is no interband tunneling, the electron continues in the same band from $k = +\pi/a$, losing energy until it is back at $k = 0$.

Singleton01 p.118, Grosso00 p.32

The previous discussion applies if there is no scattering, or at least the Bloch oscillation period T_B is much smaller than the average scattering time τ, $T_B \ll \tau$, or

$$\omega_B \tau \gg 1.$$

For simple lattices, $a \approx 1$Å, and $\omega_B \approx 10^{11}$sec^{-1}. Effectively Bloch oscillations do not matter. In superlattices, $a \approx 50 - 100$ Å, and $\omega_B \approx 10^{13}$ sec^{-1}. In that case Bloch oscillations may have an effect.

This problem goes away if we have scattering. In a scattering event the electron loses is k history and the average value of k after scattering is zero. Electrons in a field can thus carry a current if they scatter before they reach the top of the band.

Now let's look at conductivity in metals:

As we saw earlier, conductivity is given by

$$\sigma = \frac{ne^2\tau}{m^*}.$$

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We saw that the electron velocity is given by $\mathbf{v} = (1/\hbar)\nabla_{\mathbf{k}} E(\mathbf{k})$, i.e. electron velocity follows the gradient of energy, which is perpendicular to surfaces of constant energy, such as the Fermi surface.
If there is no external field, the number of electrons drifting in some directions is matched by an equal number of electrons drifting in the opposite direction.
If a field is applied, the electrons with $\mathbf{v}$ parallel to the external field move to slightly higher velocities, i.e. the Fermi surface is displaced by $\sim m^* v_d/\hbar$. The drift velocity is typically $v_d \sim 10^{-3}$ m/s. The Fermi velocity is $v_F \sim .01c$.

Singleton01 p.121

The relevant scattering time τ_σ is the time needed to randomize an electron's forward velocity. A suitable scattering even is shown with an arrow, scattering an electron to a state with approximately opposite momentum and velocity.

One important scattering mechanism is *phonon scattering*, i.e. electrons interacting with lattice vibrations or distortions because these distortions break the ideal periodicity of the crystal.

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There are two important possibilities:

- **Elastic**: Both phonon and electron change wavevector and energy. Energy and momentum are conserved.
- **Inelastic**: A phonon may be absorbed or emitted by an electron. Electron's wavevector and energy change.

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Singleton01 p.183

A phonon spectrum also has dispersion curves, $E(q)$. Phonons act as bosons, similar to photons. This plot is for a diatomic linear chain of atoms. In this case we have to branches

- **acoustic** $\omega \rightarrow 0$ as $q \rightarrow 0$. At low q values the relation is nearly linear with $\omega = v_{\text{sound}} q$. The lowest-frequency phonons are simply sound waves in a crystal.
- **optic** $\omega \rightarrow$finite as $q \rightarrow 0$.

These modes are illustrated in the lower figure. Both cases have the same wavelength. In the optic mode, neighboring atoms are displaced in opposite directions.

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”Lattice dynamics” ed. Wallis, London 1965

This is a measured dispersion diagram for phonon modes in GaAs, measured at 296K by neutron scattering. Labels are
L - longitudinal
T - transverse
O - optic
A - acoustic

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Singleton01 p.184,188

The Debye model allows us to estimate the number denisty of phonons as a function of temperature. The Debye temperature corresponds to a cut-off energy $k_B\Theta_D = \hbar\omega_D = \hbar c k_D$, where Θ_D is the Debye temperature.
At low temperatures, (T/Θ_D) = 0.1, 0.2, 0.5, the spectrum has a similar shape to black body radiation. $N_{ph} \propto T^3$
At high temperatures, (T/Θ_D) = 1, 5, the relation is linear with a sharp cut-off at Θ_D. $N_{ph} \propto T$.

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Singleton01 p.123

A typical phonon has an energy of $\hbar\omega \sim k_BT$. If an electron absorbs a phonon during scattering, it will gain this energy. Electrons can also emit phonons of $\sim k_BT$ energy. Note that after scattering an electron must find a lower-energy level to scatter into. There are free levels only within about k_BT of the Fermi level.

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At room temperature. For most metals, Θ_D is less than or comparable to room temperature. The phonon wavevector $q \approx$ maximum size = half the width of the Brillouin zone $\sim k_{\text{F}}$. Electron-phonon scattering can thus flip an electron to the opposite side of the Fermi surface.
$\tau_\sigma^{-1} \propto$number of phonons with $\hbar\omega \sim k_BT \propto T$.

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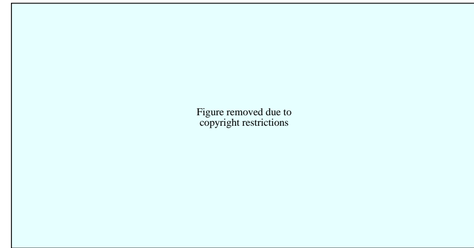
If $T \ll \Theta_D$, phonon energy $\hbar\omega \sim k_BT$ is $\ll k_B\Theta_D$ and therefore $q \ll$ Brillouin zone size, i.e. $q \ll k_F$. An inelastic scattering event can thus change the electron energy only by $\sim k_BT$. Very many scattering events are needed to absorb the excess forward velocity of an electron.
Pure forward scattering does not change the k (direction) of an electron. The effectiveness of a scattering event at randomizing an electrons wavevector is therefore dependent on the scattering angle, θ. The scattering rate has a factor $1 - \cos\theta$. For small θ,

$$1-\cos\theta \approx 1-(1-\frac{\theta^2}{2}) = \frac{\theta^2}{2} \approx \frac{q^2}{2k_F^2} \approx \frac{\omega^2}{2k_F^2 v_{\text{sound}}^2} \propto T^2,$$

because $\omega = v_{\text{sound}} q$.

We thus have a phonon number proportional to T^3 and a factor proportional to T^2, giving $\tau_\sigma \propto T^{-5}$.

The $\sigma \propto T^{-5}$ is rarely seen. There are several reasons:



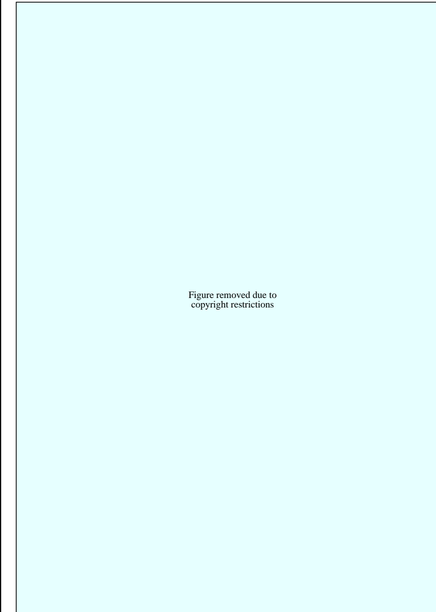
Singleton01 p.124

The k-space is periodic. It is possible for a small q to scatter an electron into a neighboring Brillouin zone (*umklapp scattering*). If viewed in the first zone, change in k is very small (A to B). If mapped to a single zone, the change can be very large (A to C).

The original assumption was that wavevectors of similar size correspond to similar velocities. This is true for a circular Fermi surface. For a complex Fermi surface shape or if interband scattering can occur, this is not true.

At very low temperatures or dirty metals, phonon scattering becomes negligible. In that case only impurity or defect scattering remains. In impurity scattering a single event can randomize the k of an electron.

Conclusions for metals:

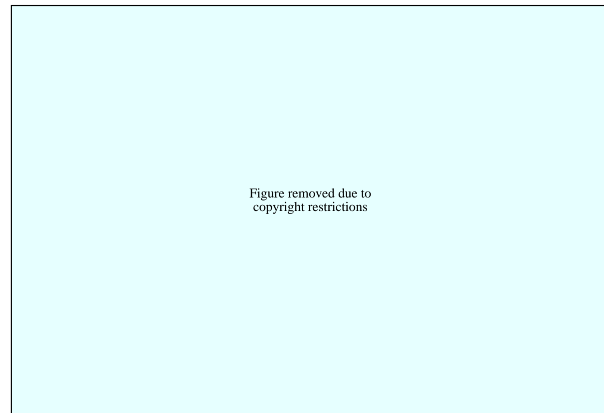


Rosenberg, "Low Temperature Solid State Physics", 1963

Temperature (scatterer)	σ
very low (impurities)	$\sigma \sim$ const.
$T \sim \Theta_D/10$ (phonons)	$\sigma \propto T^{-5}$
$T \geq \Theta_D$ (phonons)	$\sigma \propto T^{-1}$

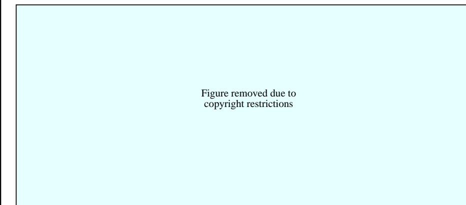
One last note:

Electron-electron scattering is not significant in metals, because initial and final states must be within $k_B T$ of E_F and wavevectros must be close to k_F. Energy and momentum must also be conserved. It is important when

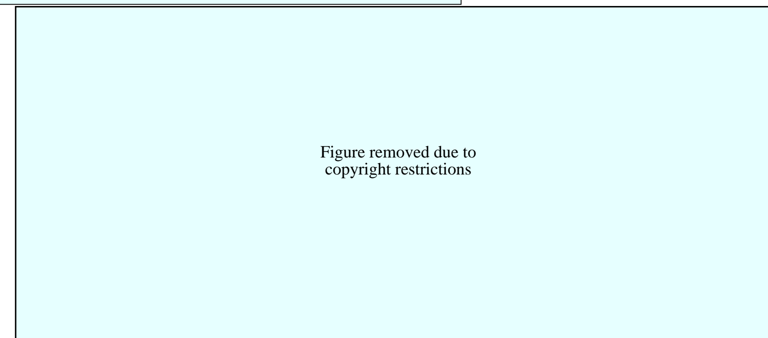


- Fermi surface has a complicated shape, so that conservation laws can apply for a variety of scattering processes.
- The density of states is very large at the energy and the effective mass is very large. This increases the number of available initial and final states. Important in transition metals and heavy fermion systems.

Semiconductors:



If the band structure of a material has a gap and the Fermi level is within this gap (a band is exactly full), we would have an insulator or a semiconductor. If there is no gap, we would have a metal.



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Start with traditional semiconductors: Si, Ge, GaAs, CdTe, etc. with the zinc blende structure.

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In both Si and Ge two bands meet at the top of the valence band at the center of the Brillouin zone (Γ point). Only the heavy holes matter, because their band is very flat and thus gives a very much higher density of states than the light holes.

Thermal excitation can occur between the highest point of the valence band and the lowest point of the conduction band (at 300K anyway, $E = k_B T$, $k_B = 8.6 \times 10^{-5}$ eV/K, 300K $\propto$ 25 meV).

Singleton01 p.50

An obvious way of characterizing the gap is to measure optical absorption. Photons with energy $h\nu \sim E_g \sim 0 - 2$ eV have wavevectors $\ll$ than a typical Brillouin zone size. A transition from valence to conduction band is thus essentially vertical in k space.

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The transition probablity is largest when the density of states (full or empty) is large in both initial and final states. This happens if conduction and valence bands are approximately parallel.

Both Si and Ge are indirect gap semiconductors. The smallest energy separation is not vertical in k-space.

Absorption is only possible if the extra k comes from somewhere, such as lattice phonons.

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Optical absorption of Ge at 300K and 77K. The indirect transition is visible at a lower energy, but intensity is 100× smaller than the direct transition. The indirect transition is stronger at 300K (more phonons available).

Singleton01 p.52

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The gap is also a function of temperature. Thermal expansion changes the atomic distances, which causes the overlap integrals to change in the tight-binding model. This changes the band widths.

The number of mobile carriers in semiconductors depends on temperature.

The number density of electrons in energy range E to $E + \mathrm{d}E$ is

$$\mathrm{d}n = f_{\mathrm{D}}(E,T)g(E)\mathrm{d}E,$$

where f_{D} is the Fermi-Dirac distribution function

$$f_{\mathrm{D}} = \frac{1}{\mathrm{e}^{\frac{E-\mu}{k_{\mathrm{B}}T}} + 1},$$

$g(E)$ is the density of states, and μ is the chemical potential. The Fermi level (i.e. μ) is within the gap and thus the occupancy of conduction band levels is $\ll 1$. This means that $(E-\mu) \gg k_{\mathrm{B}}T$ and we can approximate the F-D distribution

$$f_{\mathrm{DC}} \approx \frac{1}{\mathrm{e}^{\frac{E-\mu}{k_{\mathrm{B}}T}}} = \mathrm{e}^{-\frac{E-\mu}{k_{\mathrm{B}}T}}.$$

The chance of having a hole in the valence band is $1 - f_{\mathrm{DV}}$. In valence band $(E - \mu)$ is negative and $|E - \mu| \gg k_{\mathrm{B}}T$

$$1 - f_{\mathrm{DV}} = 1 - (1 + \mathrm{e}^{\frac{E-\mu}{k_{\mathrm{B}}T}})^{-1} \approx 1 - (1 - \mathrm{e}^{\frac{E-\mu}{k_{\mathrm{B}}T}}) = \mathrm{e}^{-\frac{\mu-E}{k_{\mathrm{B}}T}}$$

As we saw earlier, close to a band bottom (or top) the dispersion curve is parabolic and we can use a single scalar effective mass

$$g_c = C m_c^{*\frac{3}{2}} \sqrt{E - E_c}$$

and

$$g_v = C m_{hh}^{*\frac{3}{2}} \sqrt{E_v - E},$$

where $C = (1/2\pi^2)(2/\hbar^2)^{3/2}$. We can now calculate the carrier density in the conduction band

$$n = \int_{E_c}^{\infty} f_{\mathrm{DC}}\, g_c\, \mathrm{d}E \approx C m_c^{*\frac{3}{2}} \int_{E_c}^{\infty} \sqrt{E - E_c}\, \mathrm{e}^{-\frac{E-\mu}{k_{\mathrm{B}}T}}\, \mathrm{d}E$$

We can substitute $y = (E - E_c)/(k_{\mathrm{B}}T)$ and get

$$n \approx C(m_c^* k_{\mathrm{B}} T)^{\frac{3}{2}} \mathrm{e}^{-\frac{E_c-\mu}{k_{\mathrm{B}}T}} \int_0^{\infty} y^{\frac{1}{2}} \mathrm{e}^{-y}\, \mathrm{d}y.$$

Note that this is a table integral

$$\Gamma(p) = \int_0^{\infty} y^{p-1} \mathrm{e}^{-y}\, \mathrm{d}y$$

and the Gamma function recursion rules

$$\Gamma(p) = p\,\Gamma(p-1)$$
$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$$

$$n \approx C(m_c^* k_{\mathrm{B}} T)^{\frac{3}{2}} \mathrm{e}^{-\frac{E_c-\mu}{k_{\mathrm{B}}T}} \int_0^{\infty} y^{\frac{1}{2}} \mathrm{e}^{-y}\, \mathrm{d}y.$$

The integral is simply a constant, giving us the desired density

$$n = N_c \mathrm{e}^{-\frac{E_c-\mu}{k_{\mathrm{B}}T}}.$$

In a similar way we calculate the hole density in the valence band

$$p = \int_{-\infty}^{E_v} (1 - f_{\mathrm{DV}})\, g_v\, \mathrm{d}E \approx C m_{hh}^{*\frac{3}{2}} \int_{-\infty}^{E_v} \sqrt{E_v - E}\, \mathrm{e}^{-\frac{\mu-E}{k_{\mathrm{B}}T}}\, \mathrm{d}E.$$

Similar integration yields

$$p = N_v \mathrm{e}^{-\frac{\mu-E_v}{k_{\mathrm{B}}T}}.$$

N_c is the number density of accessible states at the conduction band bottom
N_v is the number density of accessible states at the valence band top.
Numerically

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

This shows that the maximum carrier concentration in a nondegenerate semiconductor is around 10^{19} carriers/cm^3 if m_c/m and m_v/m are around unity. (True in simple semiconductors, not really for oxides).

Now n and p contain the chemical potential, which we don't know. Their product, however

$$np \approx N_c N_v \mathrm{e}^{-\frac{E_g}{k_{\mathrm{B}}T}} = W T^3 \mathrm{e}^{-\frac{E_g}{k_{\mathrm{B}}T}},$$

where $E_g = E_c - E_v$ is the energy gap. The np product is known as *the law of mass action*. It means that if we know the concentration of one type of carriers at a certain temperature, we can calculate the concentration of the other type as well.

If we assume that $n = p$, we can look what happens to the chemical potential μ.

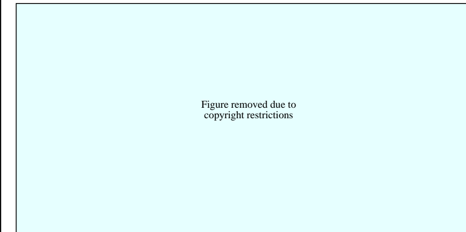
$$\frac{N_c}{N_v} = \mathrm{e}^{\frac{2\mu - E_c - E_v}{k_{\mathrm{B}}T}}$$

Note that $(N_c/N_v) = (m_c^*/m_{hh}^*)^{3/2}$. This allows us to write

$$\mu = \frac{1}{2}(E_c + E_v) + \frac{3}{4} k_{\mathrm{B}} T \ln\left(\frac{m_{hh}^*}{m_c^*}\right).$$

If $m_{hh}^* = m_c^*$, μ starts out in the middle of the gap at $T = 0$. In most cases m_{hh}^* is much larger than m_c^*, pushing μ higher.

Intrinsic semiconductors:



The equality of n and p happens in an intrinsic semiconductor, i.e. when there are no carriers donated by impurities. In that case we get the intrinsic carrier density

$$n_i = n = p = T^{3/2} W^{1/2} \mathrm{e}^{-\frac{E_g}{2k_{\mathrm{B}}T}}$$

This shows that even small changes in the gap will result in orders of magnitude changes in carrier concentration. Numerically:

$$n_i(T) = 2.5 \left(\frac{m_c}{m}\right)^{3/4} \left(\frac{m_v}{m}\right)^{3/4} \left(\frac{T}{300\mathrm{K}}\right)^{3/2} \mathrm{e}^{E_g/2k_{\mathrm{B}}T} \times 10^{19}/\mathrm{cm}^3.$$

Conductivity in a semiconductor is due to all carriers (electrons and holes)

$$\sigma = ne\mu_c + pe\mu_{hh}$$

where μ_c is the electron mobility and μ_{hh} is the hole mobility. Mobilities depend on scattering processes,

$$\mu_c = \frac{e\tau_c}{m_c^*}$$

and

$$\mu_{hh} = \frac{e\tau_{hh}}{m_{hh}^*}.$$

In most semiconductors holes have a much larger effective mass than electrons and therefore electron mobility is much larger than hole mobility. The main scattering processes are

Impurities at $T \ll \Theta_{\mathrm{D}}$. The scattering mechanism is similar to Rutheford scattering and the cross-section is proportional to E^{-2}. In our case $E \sim k_{\mathrm{B}}T$ and thus the scattering cross-section is proportional to T^{-2}, or the mean free path is proportional to T^2. The carrier speed is proportional to $E^{1/2}$, i.e. $T^{1/2}$ and thus

$$\tau \propto \frac{T^{-1/2}}{T^{-2}} = T^{3/2}.$$

Phonons at $T \sim \Theta_{\mathrm{D}}$. The number of phonons is proportional to T, leading to a mean free path proportional to T^{-1}. Speed is still proportional to $T^{1/2}$ and thus

$$\tau \propto \frac{T^{-1}}{T^{1/2}} = T^{-\frac{3}{2}}.$$

However, note that the increase of carrier density with temperature is *much* more important than scattering and, considering that

$$\sigma = ne\mu,$$

That has a much larger effect on conductivity.

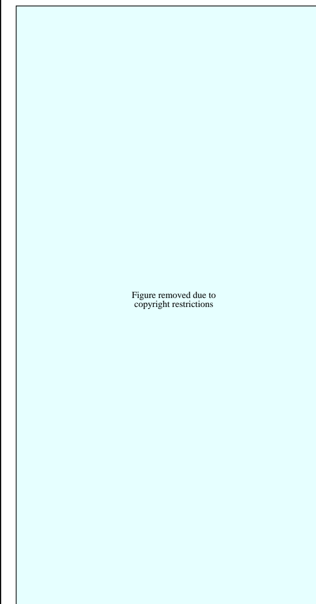
The important point is that in semiconductors (opposite to metals) *conductivity increases with temperature*.

So where is the line between a semiconductor and an insulator?

There is no sharp division. Basically a good insulator is a very wide gap semiconductor, although we often need to look at impurity levels as well. Most carriers in semiconductors (at room temperature) come from impurities.

The best insulators among oxides are non-transition metal oxides, such as SiO_2, Al_2O_3, and MgO. Most transition-metal oxides are somewhere on the boundary between being an insulator or a semiconductor.

Note that band gaps in transition metal oxides are usually very large, 3..4 eV compared to the ≈ 1 eV of traditional semiconductors. The semiconducting properties of oxides are mostly due to defects and impurities.



PRB 25 (1982) 7157

The first job is to determine the size of the gap. There are several ways of doing this. Look at the density of states for rutile-type TiO_2. The calculated band diagram shows the O $2p$ valence band and the empty Ti $3d$ and $4s$ bands.
The empty states can be probed by EELS Electron Energy Loss Spectroscopy (specific to each element, like Ti or O) and XAS X-ray Absorption Spectroscopy
These measurements look at electric-dipole allowed transitions with $\Delta l = \pm 1$. The Ti L_{23} spectrum looks at transitions starting from Ti $2p$ orbitals. The end point therefore can be a d or an s orbital. For the Ti K-edge, we start from the Ti $1s$ states. The end point should therefore be a p-orbital.
The d-peaks in the oxygen spectrum indicate a large degree of hybridization between the Ti and O levels.

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Another way to measure the gap size is to look at optical absorption spectra.
The optical absorption edge corresponds with a steep rise in photoconductivity. This shows that free carriers really are produced in the conduction band (and not bound excitons).

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Things look more complicated when polarized measurements are made. When $E \perp c$, we can see weak exciton peaks and a double edge, possibly due to an indirect transition.
When $E \parallel c$, we get a single direct edge.
This is a good example for oxides. The models explain the main features. Detailed edge structure almost never matches calculated results, often because the details of crystal structure are not known (defects, impurities, etc.).

Cox92 p.103

A listing of optical gap energes for various d^0 oxides

Binaries Compound	E_g (eV)	Ternaries Compound	E_g (eV)
($3d^0$)			
TiO_2 (rutile)	3.0	$MgTiO_3$	3.7
TiO_2 (anatase)	3.2	$SrTIO_3$	3.2
		$BaTiO_3$	3.2
		$La_2Ti_2O_7$	4.0
V_2O_5	2.2		
CrO_3	2		
($4d^0$)			
		$SrZrO_3$	5.4
Nb_2O_5	3.9	$LiNbO_3$	3.8
		$KNbO_3$	3.3
MoO_3	3.0		
($5d^0$)			
Ta_2O_5	4.2	$LiTaO_3$	3.8
		$NaTaO_3$	3.8
WO_3	2.6		

The gaps are not sharp, and decrease slightly with temperature.

In general, gaps decrease with increasing atomic number, $TiO_2 > V_2O_5 > CrO_3$.

Gap increases with heavier elements, i.e. V $<$ Nb $\sim$ Ta. Main difference is between $3d$ and $4d$, smaller difference between $4d$ and $5d$.

There is little difference between binaries and ternaries. Usually the non-transition ion in a ternary has a much higher energy, i.e. in $SrTiO_3$ the Sr $5s$ is much higher than Ti $3d$.

There are also structural differences. The corundum structure ($MgTiO_3$, $LiNbO_3$) have larger gaps than perovskites ($CaTiO_3$, $NaNbO_3$), mostly due to a different conduction band width (smaller band width gives a wider gap). rutile TiO_2 has corer- and edge-sharing octahedra (large overlap), perovskite $SrTIO_3$ has only corner-sharing octahedra (medium overlap), ilmenite $MgTiO_3$ has only partial corner sharing (low overlap).

The later elements in the transition series (that can still give d^0 compositions), such as $KMnO_4$ are nearly ionic and better viewed as a collection of individual MnO_4^- clusters. The optical absorption of a solid is nealry the same as that of a solution.

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