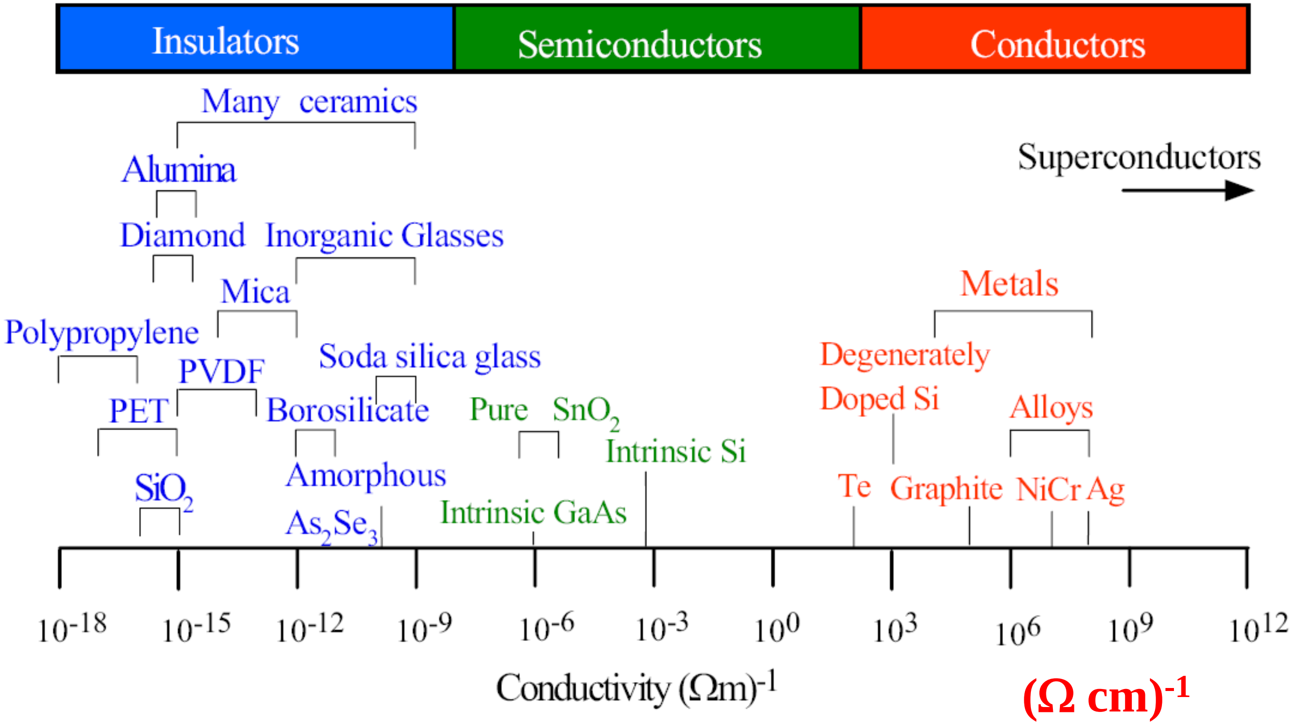
3. Electrical Conduction in Solids

3A. Classical Theory

3B. Semiclassical Theory

3C. Semiconductors

The electrical conductivity of materials varies over an unusually wide range, from values of the order of **10^6 (Ω cm)$^{-1}$ for metals** to less than 10^{-16} (Ω cm)$^{-1}$ for insulators. Semiconductors usually have a room temperature conductivity of the order of 1, although this value strongly depends on both the temperature and purity of the semiconductor. The wide range of conductivity is because it is a product of two quantities - **carrier density and mobility** (how fast the carrier can move).



Au	**~10^6 S/cm**
graphite	**~10^4 S/cm**
graphene	**~10^5 S/cm**
TCO	**~10^4 S/cm**

c-Si = 5.0×10^{22} atoms/cm^3

c-Si

μ_e = 1400 cm^2/$V\cdot s$

μ_h = 500 cm^2/$V\cdot s$

Low carrier density
Low mobility

Medium carrier density
High mobility

High carrier density
High mobility

3A. Classical Theory (Bube Ch. 9 or Kasap Ch. 2)

3A.1. Drude Model and Ohm's Law

3A.2. Temperature Dependence of Resistivity

3A.3. Matthiessens's Rule

3A.4. Hall Effect

3A.5. Ionic Conduction

Electrical conduction is essentially about how electrons move under the external electromagnetic fields. In principle, the phenomena can be described accurately by solving Schrödinger equation under the external field. However, it is a practically impossible job.

Instead, we start with a simple but useful classical theory, and apply the results in understanding various experiments. In 1900, Drude suggested a conductivity model in which electrons behave like a classical free particle with certain position and momentum, which is called the Drude model. It was long before the quantum mechanics was known, but surprisingly, his model well addressed several essential features of electrical conduction even though the original model contained false assumptions. For example, he thought that every particle is like gas atom (electron gas) with mean average energy of 3/2 *kT*. Nevertheless, many assumptions in his theory were supported by quantum mechanics later. The Drue model presented here is a modified version to be consistent with the quantum theory of solids.

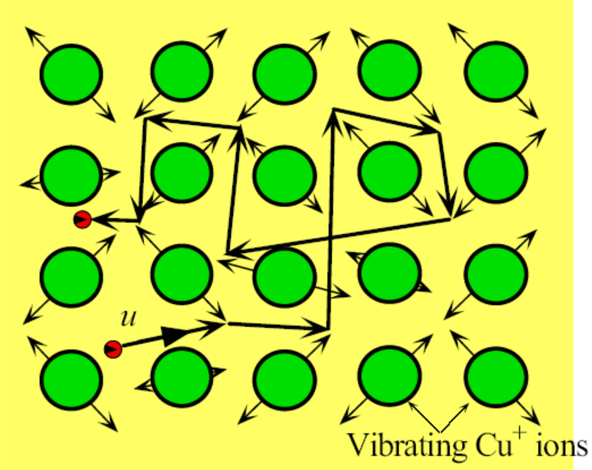
$$\sigma = ne\mu = ne^2\tau / m^*$$

free electron model

3A.1. Drude Model and Ohm's Law

Electrons accelerate under the electrical bias. If there is no barrier, the velocity of the electron will increase indefinitely, resulting in the infinite conductivity. Of course, this does not happen in real materials (except for superconductors).

Electrons **collide or scatter** with some barriers. When electrons are in the solid in which atoms are perfectly ordered, electrons do not scatter (this will be demonstrated later in the quantum approach). When lattice vibrates from the equilibrium points (i.e., in the presence of phonons) or lattice imperfections such as impurity exist, the electron will collide with them. This is the starting point of the Drude model. The Drude model in this chapter mainly concerns nearly free-electron metals, but the key concept is quite universal and applicable to semiconducting system as well.



Assumptions in the Drude model:

- In the absence of external fields, conduction electron in the metal moves randomly with a mean speed *u*: (On average, there is no net motion of electrons: $\boldsymbol{\langle u \rangle = 0}$. Here the average is over electrons in the system at a certain instance and/or over long time for an electron.) As will be shown later, the conduction is mainly mediated by electrons at the Fermi level, the mean speed of conduction electrons is typically ~10^8 cm/s (Fermi velocity).
- The electrons are scattered (change of direction) by lattice vibration or imperfections. (When atoms are periodic and static, as in 0 K, there is no scattering). The scattering among electrons is ignored.
- After collision, the velocity information is completely lost and electrons scatter in a random direction with the mean speed of *u*. That is to say, one scattering event randomize the velocity. This also means that the scattering is inelastic.

Note that the scattering events occur in the stochastic (random) manner. The mean time between collisions or scattering events is noted as τ, which is also called as **relaxation time** or **collision time**.

$1/\tau$, the inverse of τ, corresponds to the mean frequency of collisions. $\ell = u\tau$ is called the **mean free path** (length), and indicates the length over which the electron does not experience any collision.

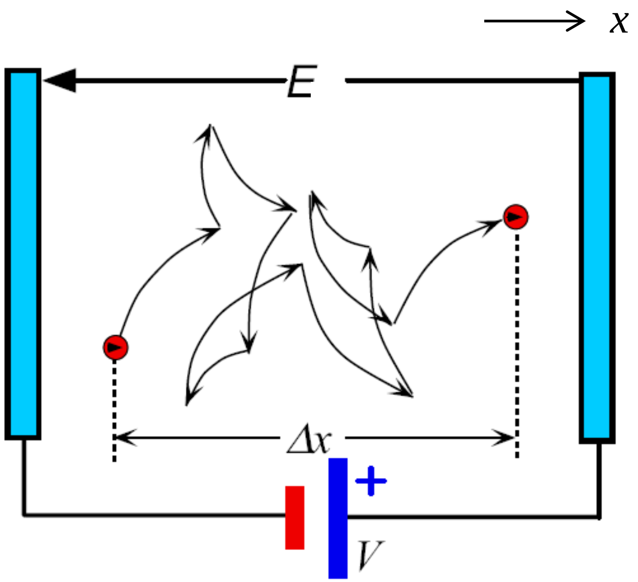
Next, we introduce an external electric field along $-x$ direction ($\mathbf{E} = -E\hat{x}$). Electrons feel the force $\mathbf{F} = eE\hat{x}$ and accelerate along x direction. Note that the accelerated component is lost after collision according to the assumption. Let's consider a certain instance. The velocity of each electron is given as follows:

initial velocity from the last collision

$$\mathbf{v}_i = \mathbf{u}_i + \frac{eE\hat{x}}{m}\Delta t_i$$

velocity of i^{th} electron

time elapsed from the last collision



This approach is called the **relaxation-time approximation**.

We then take the average over the whole electrons in the system.

$$\langle \mathbf{v}_i \rangle = \langle \mathbf{u}_i \rangle + \frac{eE\hat{x}}{m} \langle Dt_i \rangle$$

u_i = initial velocity from the last collision

Since velocity after collision is random, $\langle u_i \rangle$ is equal to zero. $\langle \Delta t_i \rangle$ is the mean time after collision and is equal to τ. (Drude mistakenly thought that this is τ/2 but the proof in the next slide shows that it is τ.)

$$\langle \mathbf{v}_i \rangle = \frac{eEt\,\hat{x}}{m} = \mathbf{v}_\mathrm{d} = v_\mathrm{d}\hat{x}$$

The remaining velocity $\mathbf{v}_\mathrm{d}$ is called the drift velocity.

$$\vec{v}_d \equiv \mu\vec{E}$$

$$v_\mathrm{d} = \frac{et}{m}E = m_\mathrm{d}E$$

The proportional coefficient μ_d is called the (drift) mobility. It determines the average speed under the electric field and heavily affect the device speed. In general, mobility is a tensor; $\mathbf{v}_\mathrm{d} = \overleftrightarrow{\mu}\mathbf{E}$ but we consider a isotropic case where $\overleftrightarrow{\mu} = \mu\overleftrightarrow{I}$.

Proof of $\langle \Delta t_i \rangle = \tau$

τ or $\tau/2$ **(skip)**

$1/\tau$: mean probability per unit time that an electron is scattered. (mean frequency of collisions)
$N(t)$: the number of unscattered electron at time t among N_0 electrons in the beginning.

$$dN = -N\left(\frac{1}{\tau}\right)dt \rightarrow N = N_0 \exp\left(-\frac{t}{\tau}\right)$$

$$\frac{N}{N_0} = \exp\left(-\frac{t}{\tau}\right) = P(t)$$

$P(t)$: probability that the electron will have no collision during t seconds after collision.

Probability that the collision occurs between t and $t + dt$:

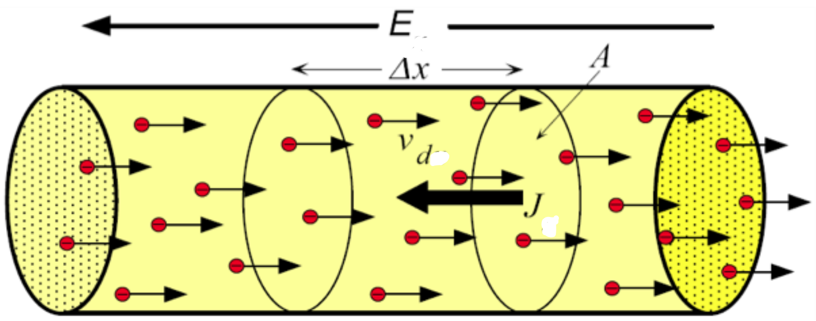
$$P(t) - P(t+dt) = \exp\left(-\frac{t}{\tau}\right) - \exp\left(-\frac{t+dt}{\tau}\right) = \frac{dt}{\tau}e^{-t/\tau} = Q(t)\,dt$$

$$\bar{t} = \int_0^\infty tQ(t)dt = \int_0^\infty \frac{t}{\tau}e^{-t/\tau}\,dt = \tau$$

Therefore, the average time for the next collision is τ. The average time for the previous collision is also τ.

Flux *J* = amount of property through unit area & unit time

Therefore, all the electrons move with the same drift velocity on average. Consider a wire lying along the direction of the electric field with the cross-sectional area of *A* and the free electron density of *n*. If the charge of *Δq* passes through *A* for the time duration of *Δt*,



$$J = \frac{\Delta q}{A\Delta t} = \frac{enAv_\mathrm{d}\Delta t}{A\Delta t} = env_\mathrm{d} = en\mu_\mathrm{d}E = \sigma E$$

$$v_\mathrm{d} = \frac{e\tau}{m}E = \mu_\mathrm{d}E$$

from ppt 3A-6

$$\sigma = en\mu_\mathrm{d} = \frac{e^2 n\tau}{m} : \text{ conductivity}$$

If the whole length of the wire is *L*, the voltage between two ends is $V = EL$. The current is $I = JA = \sigma EA$.

$$\rightarrow \frac{V}{I} = \frac{L}{A\sigma} = R \quad \text{(Ohm's law)}$$

R is the resistance. The unit of *R* is Ohm (Ω) in SI unit. Since *R* is proportional to *L* and inverse to *A*, we can normalize it to obtain a quantity intrinsic to the material, which is called the resistivity ρ.

$$\rho = R\frac{A}{L} = \frac{1}{\sigma}$$

Example: Consider **fcc Cu** at room temperature. The mass density (d) is 8.96 g cm^{-3} and atomic mass (M_{at}) is 63.5 g mol^{-1}. When the measured conductivity is $\sigma = 5.9\times10^{5}\ \Omega^{-1}\mathrm{cm}^{-1}$, obtain the following quantities

$$\boldsymbol{\sigma = ne\mu = ne^2\tau/m^*}$$

$$\boldsymbol{\upsilon_d = \mu E}$$

1. **Electron Mobility**

$$\sigma = en\mu_d$$

n = carrier density = number of electrons per unit volume

= number of Cu atoms per unit volume

(Cu yields one conduction electron)

Cu: [Ar]3d^{10}4s^{1}

$$= \frac{d}{M_{at}/N_A} = 8.5\times 10^{22}\ \text{electrons cm}^{-3}$$

$$\mu_d = \frac{\sigma}{en} = 43.4\ \mathrm{cm^2/V\cdot s}$$

Ideal Gas at 1 atm + 300 K

$v\,\tau$ = 300 nm separation = 3 nm

v = 500 m/s τ = 1 ns (= 0.5 ns)

2. **Collision Time** and **Mean Free Path** $\tau = \dfrac{\mu_d m_e}{e} = 2.5\times10^{-14}\,s = 25\ \text{fs}$

$$u \sim 1.5\times10^{6}\ \text{m/s} \rightarrow \ell = 37\ \text{nm} \leftarrow$$ **Fermi velocity**

3. for E = 10^2 V/cm, $\boldsymbol{v_d =}$?

$$u_d = \mu_d E = 43.4\ \mathrm{cm^2/Vs} \times 100\ \mathrm{V/cm} = 4340\ \mathrm{cm/s} = 43.4\ \mathrm{m/s}$$ **much smaller than the Fermi velocity**

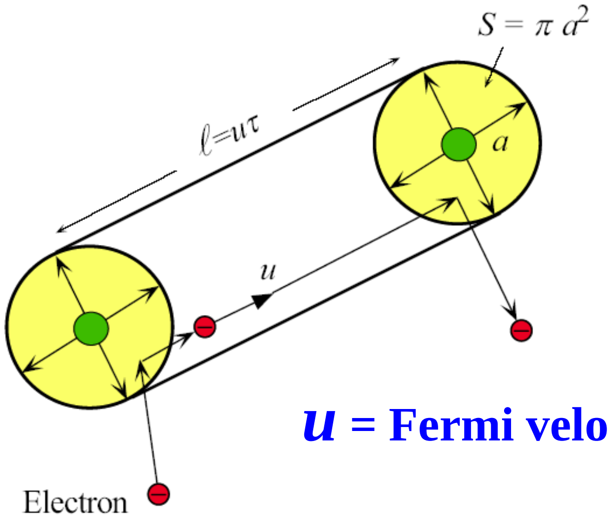
Note: It is incorrect that all the free electrons contribute to conduction because **only electrons near the Fermi level** do so. Surprisingly, the Drude formula for the conductivity is **exactly correct due to the proper cancellation**. (You will see this later. He should be a very lucky man.) Therefore, the quantities obtained in the above are all valid.

3A.2. Temperature Dependence of Resistivity

There are various sources of electron scattering which gives rise to resistivity. There are two contributions that are dominant in most materials: lattice vibrations (phonons) and lattice imperfections. In this section, we deal with the first contribution, lattice vibrations. The lattice atoms vibrate more energetically at higher temperatures, producing the temperature-dependent component of conductivity or resistivity (σ_T or ρ_T).

The figure on the right illustrates scattering of an electron from the thermal vibrations of the atoms. The electron travels a mean distance $\ell = u\tau$ between collisions. Since the scattering cross-sectional area is S (in the volume), there must be at least one scatterer $N_s\,(Su\tau\,) = 1$, where N_s is the density of scattering centers which is on the order of approximately atomic density. Therefore,

$$t = \frac{1}{SuN_s}$$



***u* = Fermi velocity**

Suppose that each atom vibrates with the vibrational amplitude of a, $S \propto \pi a^2$. Therefore, $\tau \propto \frac{1}{a^2}$. For simplicity, we assume that each atom is bound to its own harmonic oscillator (Einstein model). Then the average kinetic energy is $\frac{1}{4} M a^2 \omega^2$, where M is the atomic mass and ω is the angular frequency of the oscillator. From the equipartition theorem, the mean kinetic energy is equal to $\frac{1}{2} kT$.

$$\underline{\rightarrow t} \propto \frac{1}{a^2} \propto \frac{1}{\underline{T}} = \frac{C}{T}$$

In quantum picture, this corresponds to the **scattering by acoustic phonons** that are easily excited at room temperatures. The perturbing potential is described by the deformation potential.

$$\boldsymbol{\sigma = ne\mu = ne^2\tau / m^*}$$

This results in the dependence of mobility on the temperature.

$$\mu_d = \frac{e}{m}\tau = \frac{eC}{mT} \qquad \rightarrow \rho_T = \frac{1}{\sigma_T} = \frac{1}{en\mu_d} = \frac{mT}{e^2 nC} = AT$$

This is called **lattice-scattering-limited conductivity** (resistivity).

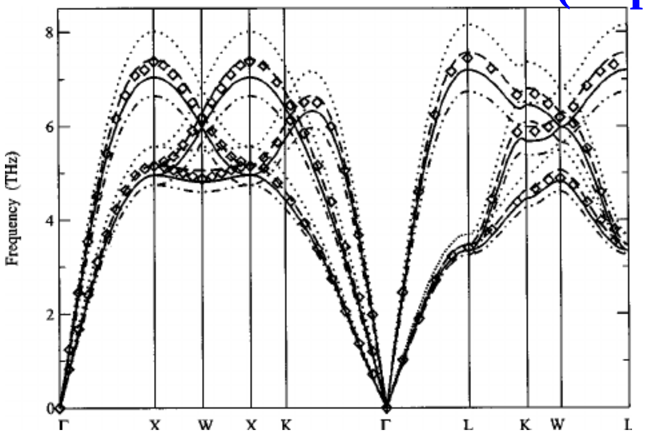
Ex. If the temperature changes from 30ºC (summer) to -10ºC (winter), what is the change in the resistance of a pure-metal wire?

$$\frac{R_{\text{summer}} - R_{\text{winter}}}{R_{\text{summer}}} = \frac{T_{\text{summer}} - T_{\text{winter}}}{T_{\text{summer}}} = \frac{(30+273) - (-10+273)}{30+273} = 0.107 \text{ or } 10.7\ \%$$

Keep in mind that the absolute temperature should be used.

(skip)

Ex. The mean speed of electron carrier in Cu is 1.5×10^{6} m/s. The vibrational frequency of Cu atoms at room T is 4×10^{12} s^{-1} (4 THz). Estimate the electron mobility [density (d) = 8.96 g cm^{-3}, M_{at} = 63.56 g mol^{-1}].



Cf. phonon band of Cu

$$N_s = \frac{dN_A}{M_{at}} = \frac{(8.96\times10^{3}\ \text{kg m}^{-3})(6.02\times10^{23}\text{mol}^{-1})}{63.56\times10^{-3}\ \text{kg mol}^{-1}} = 8.5\times10^{28}\ \text{m}^{-3}$$

$$S = \pi a^2 = \frac{2\pi kT}{M\omega^2} = \frac{2\pi(1.38\times10^{-23}\text{J K}^{-1})(300\ \text{K})}{\left(\frac{63.56\times10^{-3}\ \text{kg mol}^{-1}}{6.022\times10^{23}\ \text{mol}^{-1}}\right)(2\pi\times4\times10^{12}\text{s}^{-1})^2} = 3.9\times10^{-22}\ \text{m}^2 \quad (a = 0.11\ \text{Ang})$$

$$\tau = \frac{1}{SuN_s} = \frac{1}{(3.9\times10^{-22}\ \text{m}^2)(1.5\times10^{6}\ \text{m/s})(8.5\times10^{28}\ \text{m}^{-3})} = 2.0\times10^{-14}\ \text{s}$$

$$\mu_d = \frac{e\tau}{m_e} = 35\ \text{cm}^2/\text{V}\cdot\text{s}$$

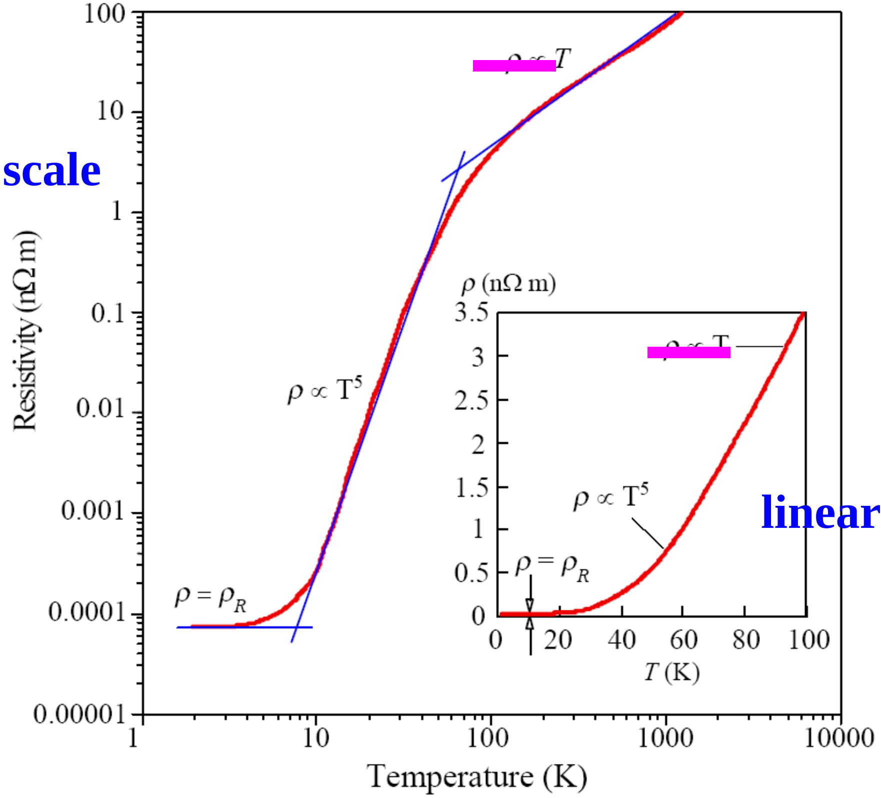
$$\sigma = en\mu_d = (1.6\times10^{-19}\text{C})(8.5\times10^{22}\text{cm}^{-3})(35\ \text{cm}^2/\text{Vs}) = 4.8\times10^{5}\Omega^{-1}\text{cm}^{-1}$$

This is in good agreement with the experimental value of $\sigma = 5.9\times10^{5}\Omega^{-1}\text{cm}^{-1}$.

Low-Temperature Behavior of Resistivity

Ex) Cu

log-log scale



~Figs. 9.2 &9.3 (Bube)

linear-linear scale

At low temperatures, the number of lattice vibrations are greatly suppressed due to the quantum nature, resulting in much more rapid decrease with temperature. (The equipartition theorem for zone-center acoustic modes does not hold.)

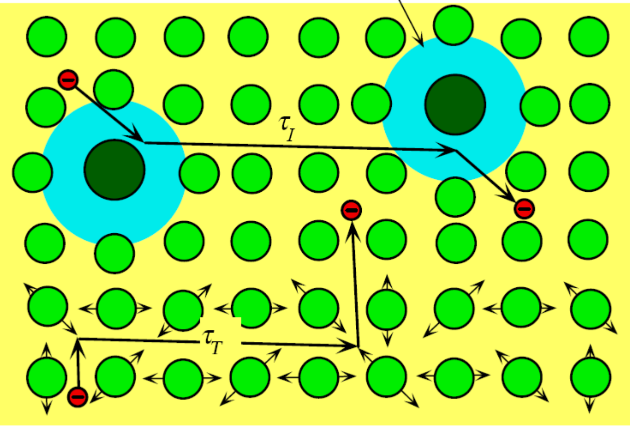
See Kasap pp 387 for explaining why ρ is proportional to T^5 at low temperatures.

3A.3. Mathiessens's Rule (Bube p. 178)

$$\sigma = ne^2\tau/m^*$$

Another major contribution to the resistivity is from the defects/impurities, which breaks the translational symmetry of crystal. **The defects can be classified into <u>point defects</u> (vacancies, interstitials, substitutional impurities) and <u>extended defects</u> (dislocations and grain boundaries).** The point defects induce local variation of potential, which cause the electron scattering.

Strained region by impurity exerts a scattering force $F = -d(PE)/dx$



Let's first assume there is one type of defects. The mean time between the collisions with the defects is τ_I. Most discussions on the phonon scattering equally apply to the impurity scattering if they exist separately. However, the **<u>two scattering mechanisms</u>** should exist simultaneously. Then how to add them? The inverse of scattering time is the scattering frequency.

$1/t_T$: scattering frequency from thermal vibrations ***- Phonons***

$1/t_I$: scattering frequency from lattice imperfections ***- Lattice Imperfections***

If the two scattering mechanisms are <u>independent</u>, the mean scattering rate is the sum of these two scattering frequency.

$$\frac{1}{t} = \frac{1}{t_T} + \frac{1}{t_I}$$

=

The total resistivity is equal to the sum of the resistivity due to the lattice scattering and due to the impurities.

This is called the Mathiessen's rule.

$1/\tau$ = mean frequency of collision

Two Scattering Mechanisms

$$\frac{1}{\tau}=\frac{1}{\tau_T}+\frac{1}{\tau_I}$$

(9.14) Bube

For the mobility $$\mu_d=\frac{e}{m}\tau \rightarrow \frac{1}{\mu_d}=\frac{m}{e}\frac{1}{\tau}=\frac{m}{e}\left(\frac{1}{\tau_T}+\frac{1}{\tau_I}\right)=\frac{1}{\mu_T}+\frac{1}{\mu_I}$$

That is to say, the drift mobility is the harmonic average of lattice-scattering-limited drift mobility (μ_T) and the impurity-scattering-limited drift mobility (μ_I).

In terms of resistivity,

$$\rho=\frac{1}{en\mu_d}=\frac{1}{en\mu_T}+\frac{1}{en\mu_I}=\rho_T+\rho_I$$

Note that ρ_I is (approximately) temperature independent and depends on the defect concentration. In general, there are several types of defects. The scattering with each defect type is independent if the density is not too high. Therefore, one can apply to Matthiesen's rule, and total resistivity is the sum of resistivity caused by each defect type. The impurity scattering remains even at low temperatures.

The concentration of equilibrium defects such as vacancies depends on the temperature. Its concentrations are typically very low so do not affect the conductivity much. Here we rather concern on the non-equilibrium defects.

$$\boldsymbol{\sigma = ne\mu = ne^2\tau/m^*}$$

Semiconductor or Electrolyte (cation/anion)

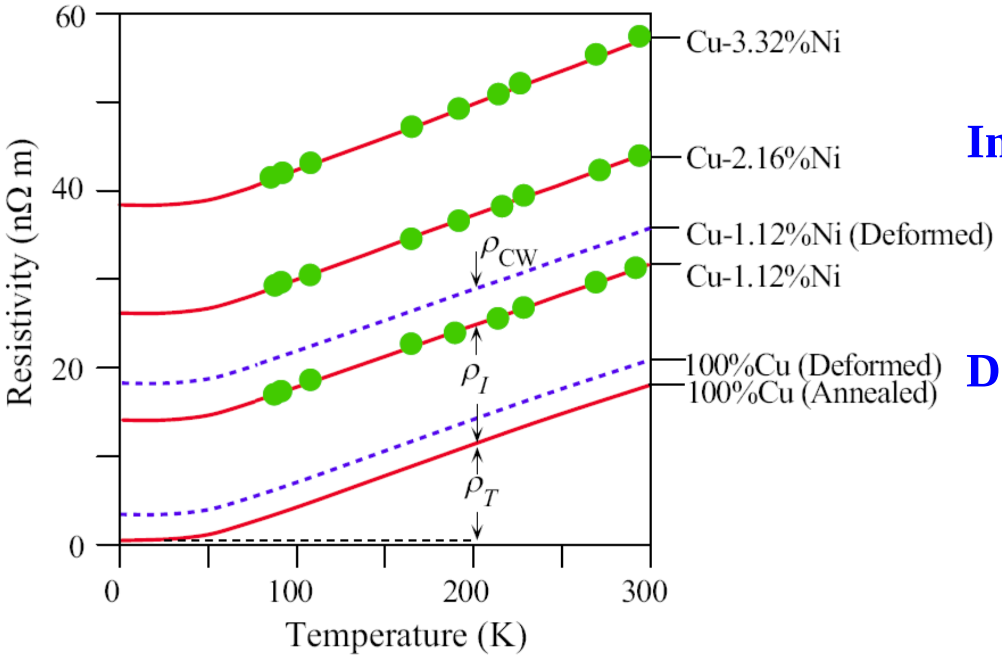
$$\sigma = n|e|\mu_e + p|e|\mu_h$$

ppt 3A-8

(9.5) Bube

Demonstration of Mathiessen's law: resistivity of Cu

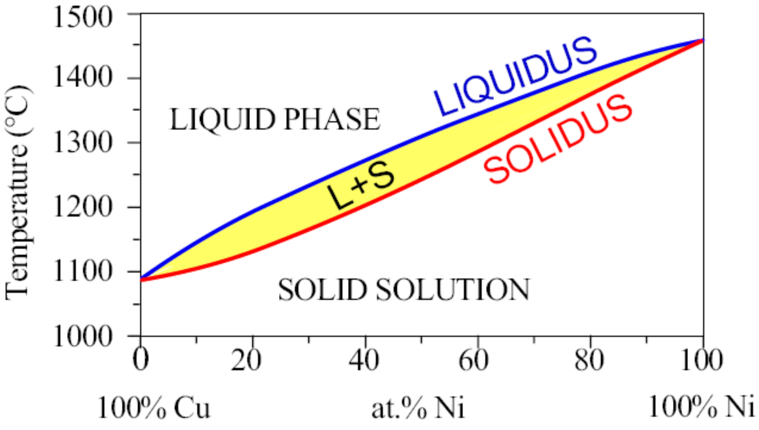
Lattice imperfections



Impurities

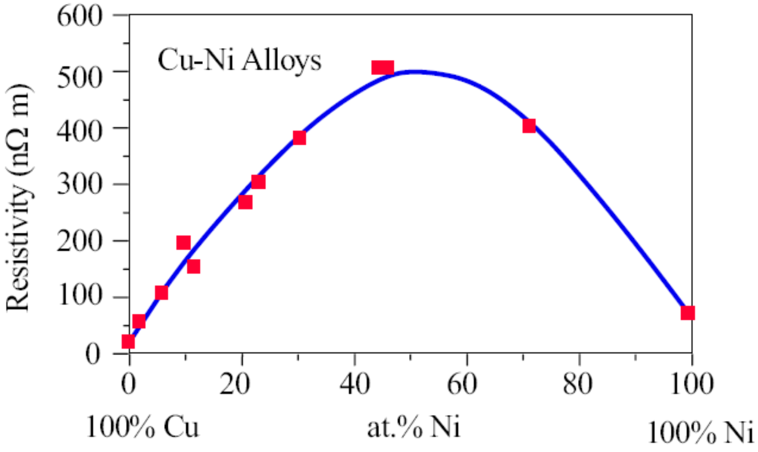
Defects

Typical temperature dependence of the resistivity of annealed and cold-worked (deformed) copper containing various amounts of Ni in atomic percentage. The deformed samples contain extended defects such as dislocations while they disappear in the annealed samples. The alloying element substitutes Cu atoms randomly so they play as impurities and scattering centers.



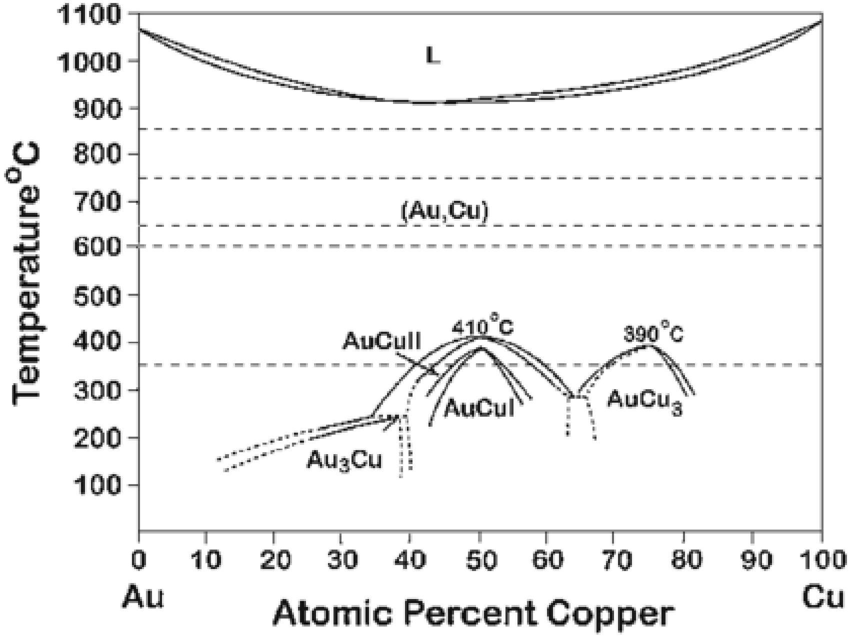
(a)

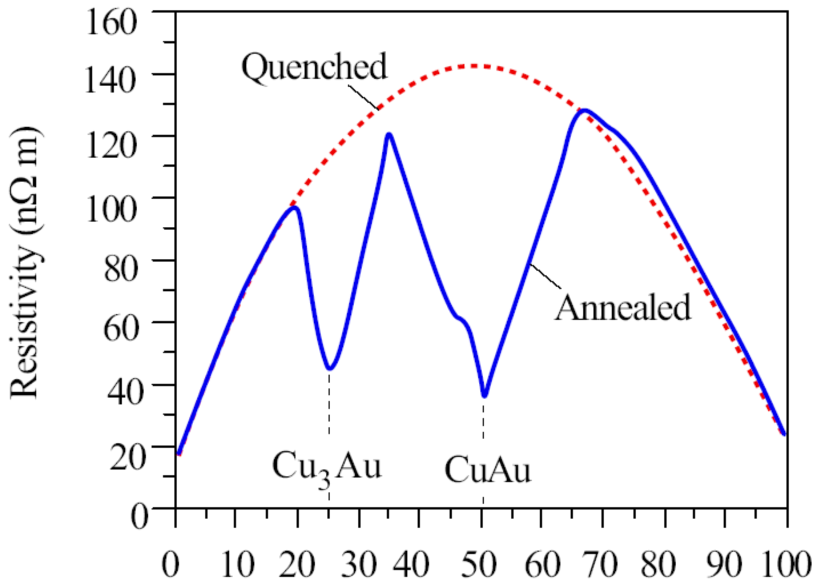
(a) Phase diagram of the Cu-Ni alloy system. Above the liquidus line, only the liquid phase exists. In the *L* + *S* region, the liquid (*L*) and solid (*S*) phases coexist, whereas below the solidus line, only the solid phase (a solid solution) exists.

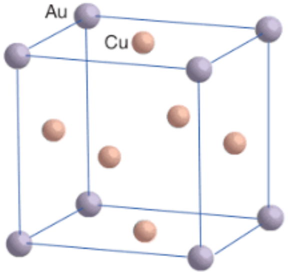


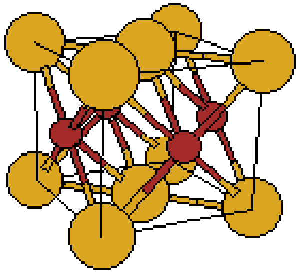
(b)

(b) The resistivity of the Cu-Ni alloy as a function of Ni content (at. %) at room temperature. It is peaked at approximately 1:1 composition where the randomness is maximized.





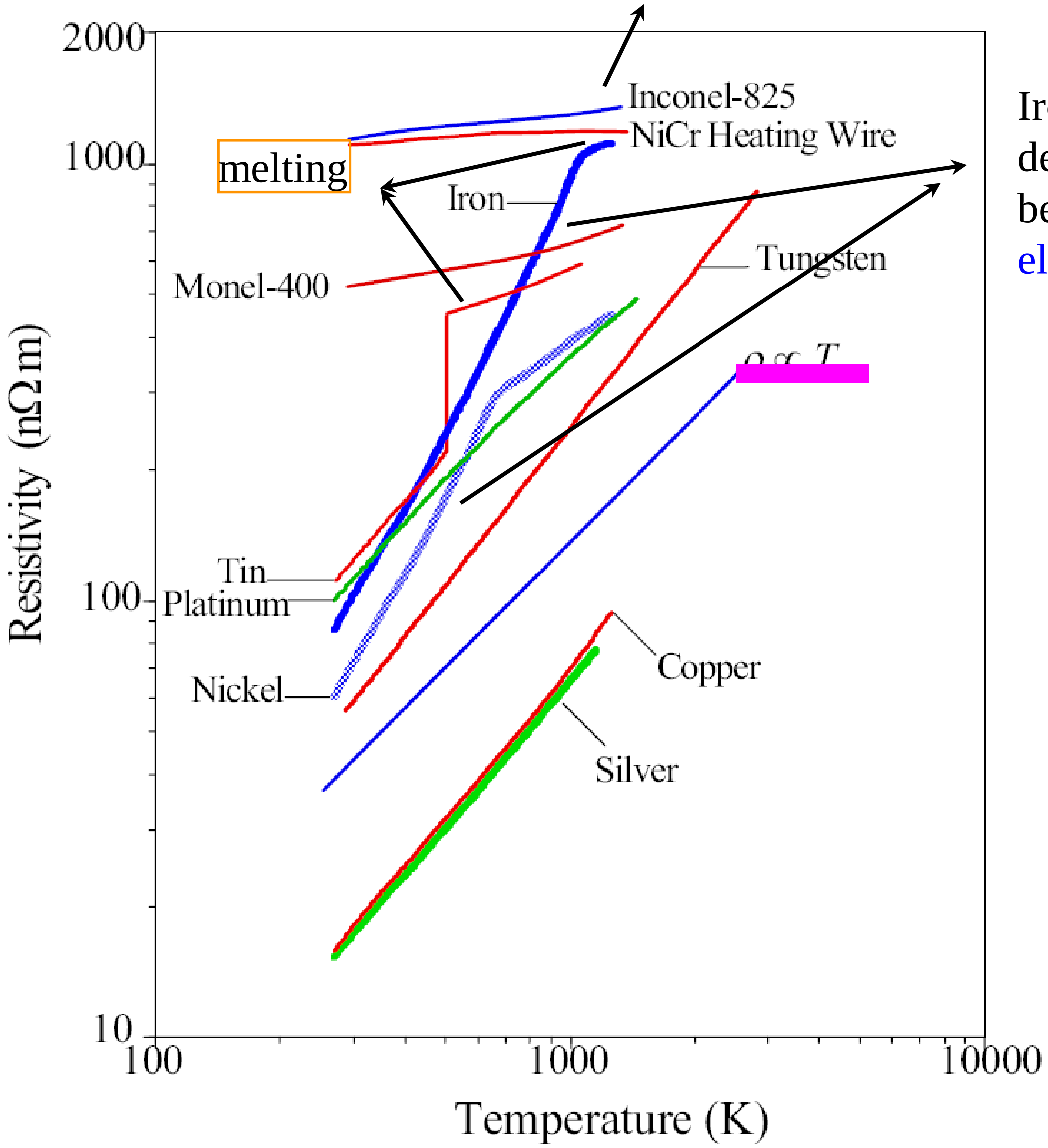




Electrical resistivity vs. composition at room temperature in Cu-Au alloys. The quenched sample (dashed curve) is obtained by quenching the liquid, and the Cu and Au atoms are randomly mixed. When the quenched sample is annealed or the liquid is slowly cooled (solid curve), certain compositions (Cu_3Au and CuAu) result in an ordered crystalline structure in which the Cu and Au atoms are positioned in an ordered fashion in the crystal and the scattering effect is reduced.

Temperature Dependence of Resistivity in Various Metals

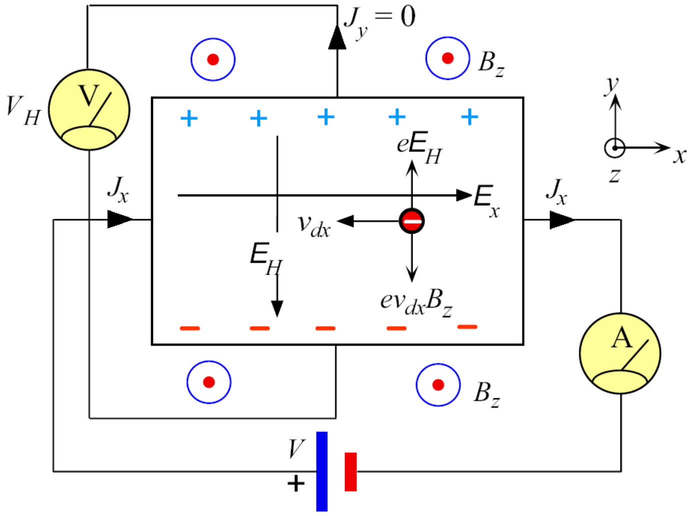
large residual resistivity for alloys: small T-dependence



Iron and nickel show strong deviations from the linear behavior due to the electron-magnon scattering.

3A.4. Hall Effect

In the Hall measurement, the device is under the uniform electric and magnetic fields that are perpendicular to each other. Electrons experience the Lorentz force $\mathbf{F} = q(\mathbf{E} + \mathbf{v}\times\mathbf{B})$. The magnetic field deflects the electron such that electrons accumulate at the bottom and positive ions (stripped with electrons) remain at the top. The charge separation continues until the Hall field E_H between them balances the Lorentz force by the magnetic field. The steady-state is then established and the electron flows along the external field direction. E_H for this stead-state condition can be obtained as follows:



$$eE_H = e\upsilon_{dx}B_z \qquad J_x = en\upsilon_{dx}$$

$$\rightarrow E_H = \left(\frac{1}{en}\right)J_xB_z$$

The Hall field can be measured by the voltmeter. In addition, the current density J_x can be detected by the amperemeter. The **Hall coefficient** is defined as

$$\rightarrow \text{Hall coefficient: } R_H = \frac{E_y}{J_xB_z} = -\frac{E_H}{J_xB_z} = -\frac{1}{en}$$

$$\boldsymbol{R_H = -1/nec}$$

Again, this classical result is confirmed by quantum mechanical approach (see A&M pp 235).

To measure the carrier concentration *n* experimentally.

TCO Semiconductor Metal etc.

(skip)

In addition, $|\sigma R_H| = \frac{\sigma}{en} = \frac{en\mu_d}{en} = \mu_d$ (from Drude model) $= \mu_H$: Hall mobility

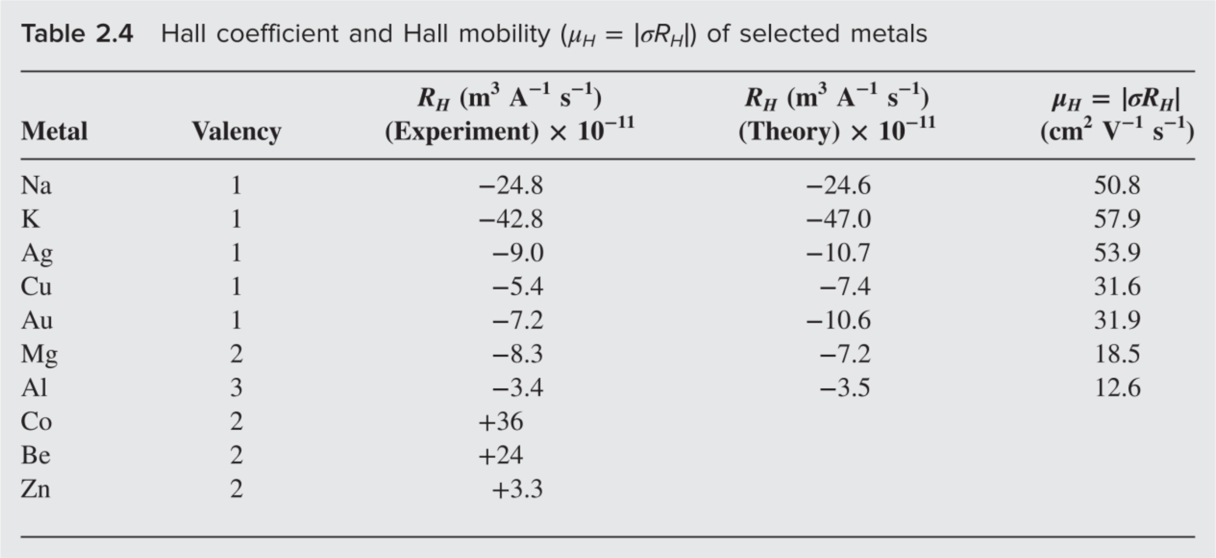
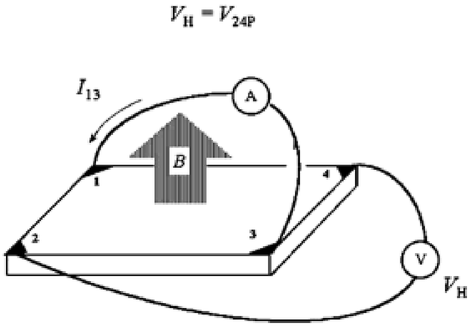


Table 2.4 Hall coefficient and Hall mobility ($\mu_H = |\sigma R_H|$) of selected metals

Metal	Valency	R_H ($m^3 A^{-1} s^{-1}$) (Experiment) × 10^{-11}	R_H ($m^3 A^{-1} s^{-1}$) (Theory) × 10^{-11}	$\mu_H = \lvert\sigma R_H\rvert$ ($cm^2 V^{-1} s^{-1}$)
Na	1	−24.8	−24.6	50.8
K	1	−42.8	−47.0	57.9
Ag	1	−9.0	−10.7	53.9
Cu	1	−5.4	−7.4	31.6
Au	1	−7.2	−10.6	31.9
Mg	2	−8.3	−7.2	18.5
Al	3	−3.4	−3.5	12.6
Co	2	+36		
Be	2	+24		
Zn	2	+3.3		

SOURCE: Hurd, C., *The Hall Coefficient of Metals and Alloys,* Plenum, New York, NY, 1972, along with other various sources.



Hall coefficients are measured typically based on van der Pauw method

The theoretical values are obtained by applying the nominal valence charges to the formula and they are in fair agreement with the experimental data. The Hall mobility for Cu is similar to the drift mobility calculated previously.

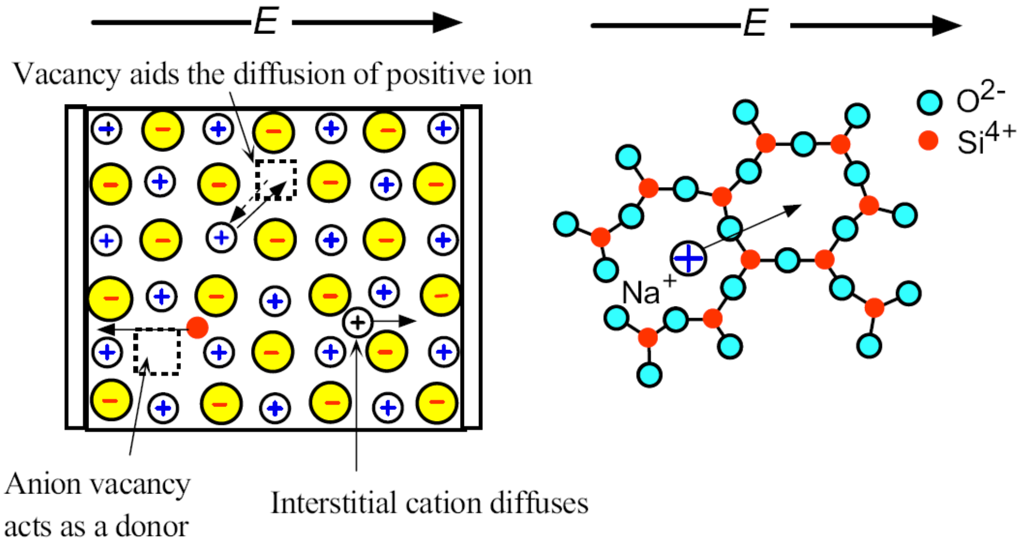
The positive values for Co, Be, and Zn indicates that the charge carrier is positively charged, which cannot be explained classically. We will see that the band structure can account for this anomaly.

3A.5. Ionic Conduction

Electrolyte: liquid & solid

Ideal Electrolyte = 100% Ionic Conductivity

In insulating ionic solids where charge carriers are negligible, ions can move under the external bias, producing electric currents.



(a) **(b)**

Possible contribution to the conductivity of ceramic and glass insulators.

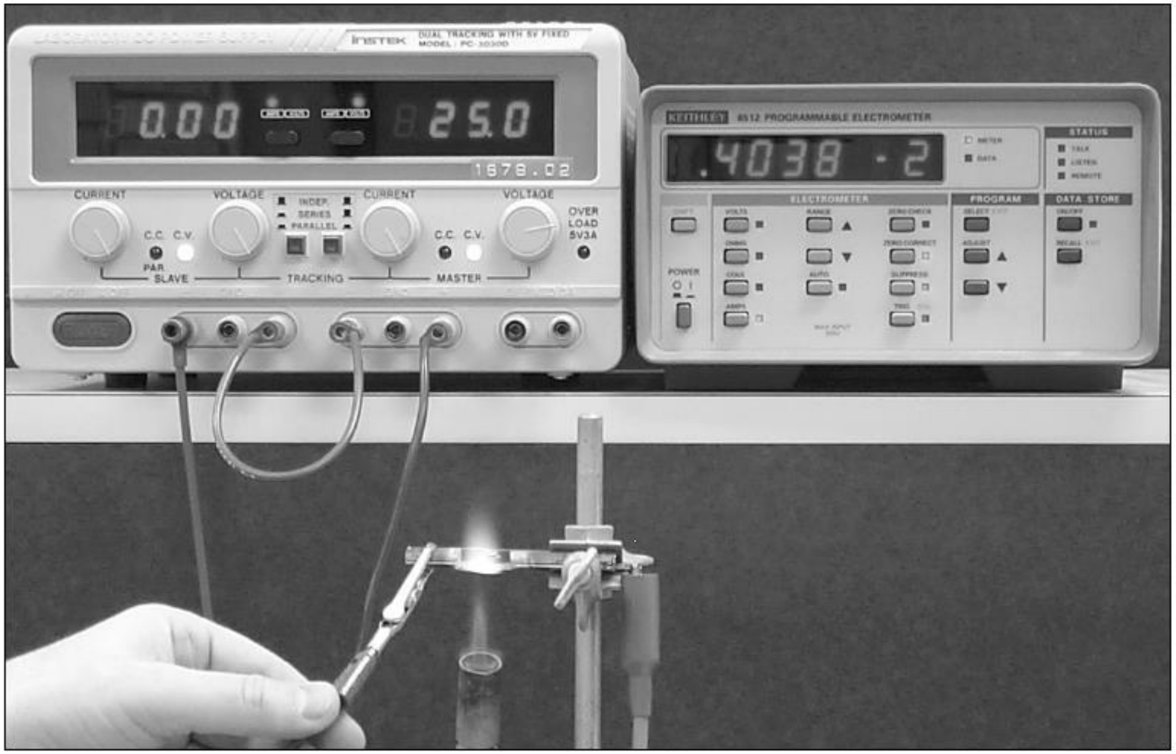
(a) Possible mobile charges in a ceramic

(b) An Na+ ion in the glass diffuses and drifts in the direction of the field

Since the creation and diffusion of atoms are thermally activated processes,

$$\sigma = \sigma_0 \exp\left(-\frac{E_\sigma}{kT}\right) \qquad E_\sigma \text{ : activation energy for conductivity}$$

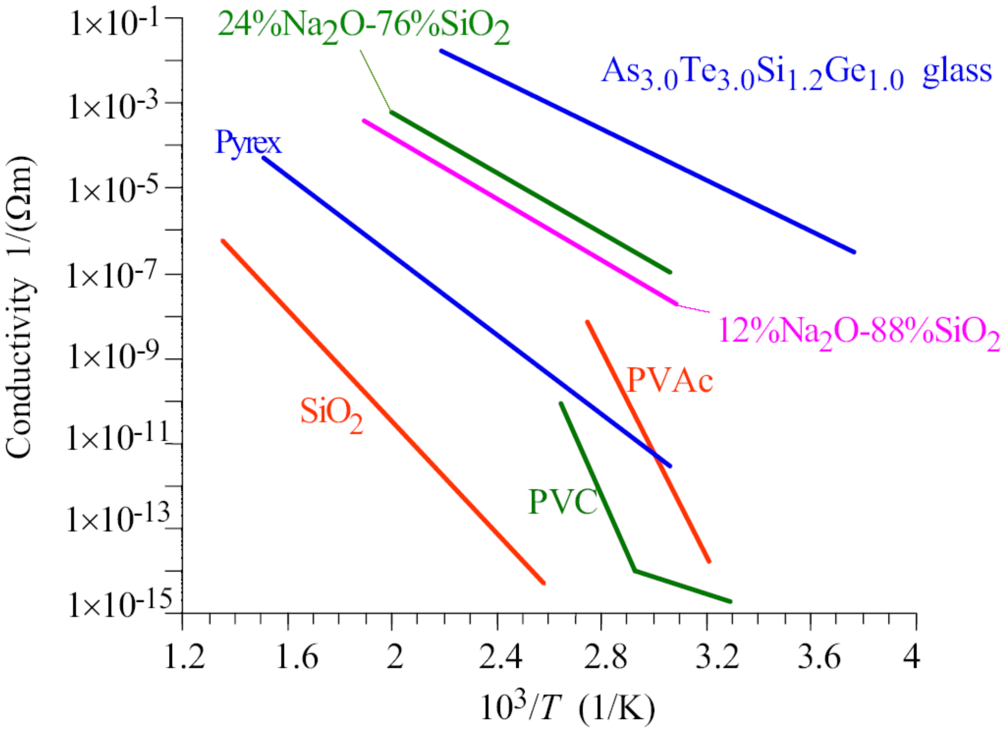
Voltage & Current Measurements with Cross Section



This soda glass rod when heated under a torch becomes electrically conducting. It passes 4 mA when the voltage is 50 V (2 × 25 V); a resistance of 12.5 kΩ! Ordinary soda glass at room temperature is an insulator but can be quite conducting at sufficiently high temperatures.

Electrical Conductivity

Conductivity for the ionic conduction exhibits a linear relationship between the log of conductivity and 1/*T*. The slope in this plot corresponds to the activation energy for diffusion divided by the Boltzmann constant.



Arrhenius-Type Temperature Dependence

Activation Enthalpy
≈ Activation Energy

Ex. E_σ for conductivity of a soda-silicate glass ($12\%\ Na_2O$-$88\%\ SiO_2$)
Slope in lnσ vs. 1/T = $-E_\sigma/k_B \rightarrow E_\sigma = 0.71$ eV
cf. E_a for diffusion of Na+ in glass: 0.65-0.75 eV

-Thu/9/24/20
- Next Class = Tue/Oct/6/20
due to Thanksgiving
- Class Exam = Tue/Oct/13/20