Electrical and Thermal Conduction in Solids

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Content

Classical theory of electrical and thermal conduction, Scattering, mobility and resistivity, temperature dependence of metal resistivity, Mathiessen's rule, Hall effect and thermal conductivity

References

Principles of Electronic Materials and Devices – S. O. Kasap
Electrical Engineering Materials – A. J. Dekker

CHAPTER

2

Electrical and Thermal Conduction in Solids: Mainly Classical Concepts

Electrical conduction involves the motion of charges in a material under the influence of an applied electric field. A material can generally be classified as a conductor if it contains a large number of "free" or mobile charge carriers. In metals, due to the nature of metallic bonding, the valence electrons from the atoms form a sea of electrons that are free to move within the metal and are therefore called conduction electrons. In this chapter, we will treat the conduction electrons in metal as "free charges" that can be accelerated by an applied electric field. In the presence of an electric field, the conduction electrons attain an average velocity, called the drift velocity, that depends on the field. By applying Newton's second law to electron motion and using such concepts as mean free time between electron collisions with lattice vibrations, crystal defects, impurities, etc., we will derive the fundamental equations that govern electrical conduction in solids. A key concept will be the drift mobility, which is a measure of the ease with which charge carriers in the solid drift under the influence of an external electric field.

Good electrical conductors, such as metals, are also known to be good thermal conductors. The conduction of thermal energy from higher to lower temperature regions in a metal involves the conduction electrons carrying the energy. Consequently, there is an innate relationship between the electrical and thermal conductivities, which is supported by theory and experiments.

2.1 CLASSICAL THEORY: THE DRUDE MODEL

The electric current density J is defined as the net amount of charge flowing across a unit area per unit time, that is,

Current density definition

$$J = \frac{\Delta q}{A\ \Delta t}$$

where Δq is the net quantity of charge flowing through an area A in time Δt. Figure 2.1 shows the net flow of electrons in a conductor section of cross-sectional area A in the presence of an applied field E_x. Notice that the direction of electron motion is opposite to that of the electric field E_x and of conventional current, because the electrons experience a Coulombic force eE_x in the x direction, due to their negative charge.

We know that the conduction electrons are actually moving around randomly[1] in the metal, but we will assume that as a result of the application of the electric field E_x, they all acquire a net velocity in the x direction. Otherwise, there would be no net flow of charge through area A.

The average velocity of the electrons in the x direction at time t is denoted $v_{dx}(t)$. This is called the **drift velocity,** which is the instantaneous velocity v_x in the x direction averaged over many electrons (perhaps, $\sim 10^{28}$ m^{-3}); that is

Definition of drift velocity

$$v_{dx} = \frac{1}{N}[v_{x1} + v_{x2} + v_{x3} + \cdots + v_{xN}] \qquad [2.1]$$

where v_{xi} is the x direction velocity of the ith electron, and N is the number of conduction electrons in the metal. Suppose that n is the number of electrons per unit volume in the conductor ($n = N/V$). In time Δt, electrons move a distance $\Delta x = v_{dx}\ \Delta t$, so the total charge Δq crossing the area A is $enA\ \Delta x$. This is valid because all the electrons within distance Δx pass through A; thus, $n(A\ \Delta x)$ is the total number of electrons crossing A in time Δt.

The current density in the x direction is

$$J_x = \frac{\Delta q}{A\ \Delta t} = \frac{enAv_{dx}\ \Delta t}{A\ \Delta t} = env_{dx}$$

This general equation relates J_x to the average velocity v_{dx} of the electrons. It must be appreciated that the average velocity at one time may not be the same as at another time, because the applied field, for example, may be changing: $E_x = E_x(t)$. We therefore allow for a time-dependent current by writing

Current density and drift velocity

$$J_x(t) = env_{dx}(t) \qquad [2.2]$$

To relate the current density J_x to the electric field E_x, we must examine the effect of the electric field on the motion of the electrons in the conductor. To do so, we will consider the copper crystal.

[1] All the conduction electrons are "free" within the metal and move around randomly, being scattered from vibrating metal ions, as we discuss in this chapter.

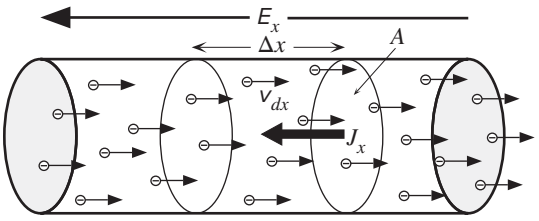


Figure 2.1 Drift of electrons in a conductor in the presence of an applied electric field.

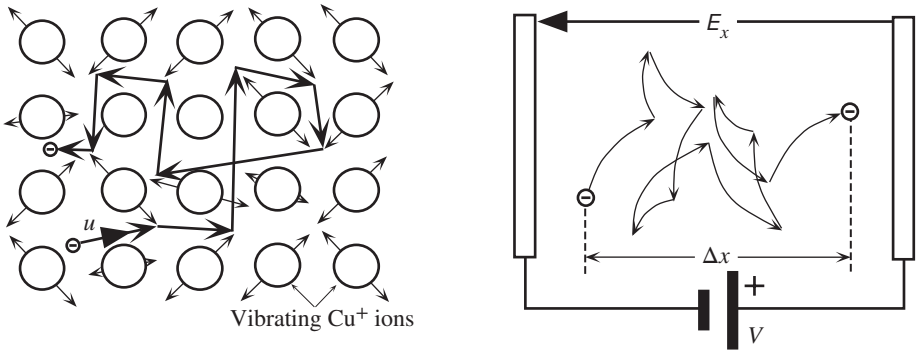
Electrons drift with an average velocity v_{dx} in the x direction.

The copper atom has a single valence electron in its 4*s* subshell, and this electron is loosely bound. The solid metal consists of positive ion cores, Cu^+, at regular sites, in the face-centered cubic (FCC) crystal structure. The valence electrons detach themselves from their parents and wander around freely in the solid, forming a kind of electron cloud or gas. These mobile electrons are free to respond to an applied field, creating a current density J_x. The valence electrons in the electron gas are therefore **conduction electrons.**

The attractive forces between the negative electron cloud and the Cu^+ ions are responsible for metallic bonding and the existence of the solid metal. (This simplistic view of metal was depicted in Figure 1.7 for copper.) The electrostatic attraction between the conduction electrons and the positive metal ions, like the electrostatic attraction between the electron and the proton in the hydrogen atom, results in the conduction electron having both potential energy *PE* and kinetic energy *KE*. The conduction electrons move about the crystal lattice in the same way that gas atoms move randomly in a cylinder. Although the average *KE* for gas atoms is $\frac{3}{2}kT$, this is not the case for electrons in a metal, because these electrons strongly interact with the metal ions and with each other as a result of electrostatic interactions.

The mean *KE* of the conduction electrons in a metal is primarily determined by the electrostatic interaction of these electrons with the positive metal ions and also with each other. For most practical purposes, we will therefore neglect the temperature dependence of the mean *KE* compared with other factors that control the behavior of the conduction electrons in the metal crystal. We can speculate from Example 1.1, that the magnitude of mean *KE* must be comparable to the magnitude of the mean *PE* of electrostatic interaction[2] or, stated differently, to the metal bond energy which is several electron volts per atom. If u is the **mean speed** of the conduction electrons, then, from electrostatic interactions alone, we expect $\frac{1}{2}m_e u^2$ to be several electron volts which means that u is typically $\sim 10^6$ m s^{-1}. This purely classical and intuitive reasoning is not sufficient, however, to show that the mean speed u is relatively temperature insensitive and much greater than that expected from kinetic molecular theory. The true reasons are quantum mechanical and are discussed in Chapter 4. (They arise from what is called the Pauli exclusion principle.)

[2] There is a theorem in classical mechanics called the **virial theorem,** which states that for a collection of particles, the mean *KE* has half the magnitude of the mean *PE* if the only forces acting on the particles are such that they follow an inverse square law dependence on the particle–particle separation (as in Coulombic and gravitational forces).



(a) A conduction electron in the electron gas moves about randomly in a metal (with a mean speed *u*) being frequently and randomly scattered by thermal vibrations of the atoms. In the absence of an applied field there is no net drift in any direction.

(b) In the presence of an applied field, E_x, there is a net drift along the *x* direction. This net drift along the force of the field is superimposed on the random motion of the electron. After many scattering events the electron has been displaced by a net distance, Δx, from its initial position toward the positive terminal.

Figure 2.2 Motion of a conduction electron in a metal.

In general, the copper crystal will not be perfect and the atoms will not be stationary. There will be crystal defects, vacancies, dislocations, impurities, etc., which will scatter the conduction electrons. More importantly, due to their thermal energy, the atoms will vibrate about their lattice sites (equilibrium positions), as depicted in Figure 2.2a. An electron will not be able to avoid collisions with vibrating atoms; consequently, it will be "scattered" from one atom to another. In the absence of an applied field, the path of an electron may be visualized as illustrated in Figure 2.2a, where scattering from lattice vibrations causes the electron to move randomly in the lattice. On those occasions when the electron reaches a crystal surface, it becomes "deflected" (or "bounced") back into the crystal. Therefore, in the absence of a field, after some duration of time, the electron crosses its initial x plane position again. Over a long time, the electrons therefore show no net displacement in any one direction.

When the conductor is connected to a battery and an electric field is applied to the crystal, as shown in Figure 2.2b, the electron experiences an acceleration in the x direction in addition to its random motion, so after some time, it will drift a finite distance in the x direction. The electron accelerates along the x direction under the action of the force eE_x, and then it suddenly collides with a vibrating atom and loses the gained velocity. Therefore, there is an average velocity in the x direction, which, if calculated, determines the current via Equation 2.2. Note that since the electron experiences an acceleration in the x direction, its trajectory between collisions is a parabola, like the trajectory of a golf ball experiencing acceleration due to gravity.

To calculate the drift velocity v_{dx} of the electrons due to applied field E_x, we first consider the velocity v_{xi} of the ith electron in the x direction at time t. Suppose

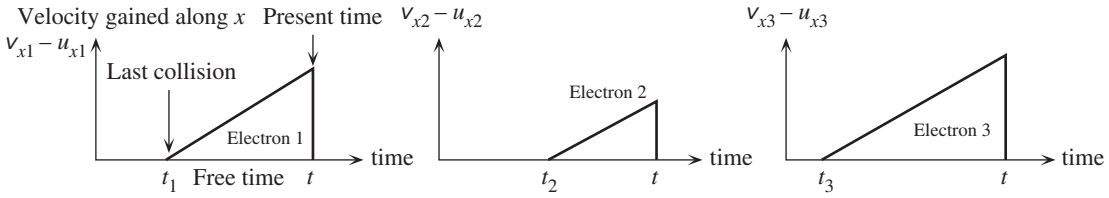


Figure 2.3 Velocity gained in the x direction at time t from the electric field (E_x) for three electrons. There will be N electrons to consider in the metal.

its last collision was at time t_i; therefore, for time $(t - t_i)$, it accelerated *free of collisions,* as indicated in Figure 2.3. Let u_{xi} be the velocity of electron i in the x direction just after the collision. We will call this the initial velocity. Since eE_x/m_e is the acceleration of the electron, the velocity v_{xi} in the x direction at time t will be

$$v_{xi} = u_{xi} + \frac{eE_x}{m_e}(t - t_i)$$

However, this is only for the ith electron. We need the average velocity v_{dx} for all such electrons along x. We average the expression for $i = 1$ to N electrons, as in Equation 2.1. We assume that immediately after a collision with a vibrating ion, the electron may move in any random direction; that is, it can just as likely move along the negative or positive x, so that u_{xi} averaged over many electrons is zero. Thus,

$$v_{dx} = \frac{1}{N}[v_{x1} + v_{x2} + \cdots + v_{xN}] = \frac{eE_x}{m_e}\overline{(t - t_i)}$$

Drift velocity

where $\overline{(t - t_i)}$ is the **average free time** for N electrons between collisions.

Suppose that τ is the mean free time, or the **mean time between collisions** (also known as the **mean scattering time**). For some electrons, $(t - t_i)$ will be greater than τ, and for others, it will be shorter, as shown in Figure 2.3. Averaging $(t - t_i)$ for N electrons will be the same as τ. Thus, we can substitute τ for $\overline{(t - t_i)}$ in the previous expression to obtain

$$v_{dx} = \frac{e\tau}{m_e}E_x \qquad [2.3]$$

Drift velocity and field

Equation 2.3 shows that the drift velocity increases linearly with the applied field. The constant of proportionality $e\tau/m_e$ has been given a special name and symbol. It is called the **drift mobility** μ_d, which is defined as

$$v_{dx} = \mu_d E_x \qquad [2.4]$$

Definition of drift mobility

where

$$\mu_d = \frac{e\tau}{m_e} \qquad [2.5]$$

Drift mobility and mean free time

Equation 2.5 relates the drift mobility of the electrons to their mean scattering time τ. To reiterate, τ, which is also called the **relaxation time,** is directly related

to the microscopic processes that cause the scattering of the electrons in the metal; that is, lattice vibrations, crystal imperfections, and impurities, to name a few.

From the expression for the drift velocity v_{dx}, the current density J_x follows immediately by substituting Equation 2.4 into 2.2, that is,

Ohm's law

$$J_x = en\mu_d E_x \tag{2.6}$$

Therefore, the current density is proportional to the electric field and the conductivity σ is the term multiplying E_x, that is,

Unipolar conductivity

$$\sigma = en\mu_d \tag{2.7}$$

It is gratifying that by treating the electron as a particle and applying classical mechanics ($F = ma$), we are able to derive Ohm's law. We should note, however, that we assumed τ to be independent of the field.

Drift mobility is important because it is a widely used electronic parameter in semiconductor device physics. The drift mobility gauges how fast electrons will drift when driven by an applied field. If the electron is not highly scattered, then the mean free time between collisions will be long, τ will be large, and by Equation 2.5, the drift mobility will also be large; the electrons will therefore be highly mobile and be able to "respond" to the field. However, a large drift mobility does not necessarily imply high conductivity, because σ also depends on the concentration of conduction electrons n.

The mean time between collisions τ has further significance. Its reciprocal $1/\tau$ represents the **mean frequency of collisions** or **scattering events;** that is, $1/\tau$ is the mean probability per unit time that the electron will be scattered (see Example 2.1). Therefore, during a small time interval δt, the probability of scattering will be $\delta t/\tau$. The probability of scattering per unit time $1/\tau$ is time independent and depends only on the nature of the electron scattering mechanism.

There is one important assumption in the derivation of the drift velocity v_{dx} in Equation 2.3. We obtained v_{dx} by averaging the velocities v_{xi} of N electrons along x at one instant, as defined in Equation 2.1. The drift velocity therefore represents the average velocity of *all* the electrons along x at one instant; that is, v_{dx} is a number average at one instant. Figure 2.2b shows that after many collisions, after a time interval $\Delta t \gg \tau$, an electron would have been displaced by a net distance Δx along x. The term $\Delta x/\Delta t$ represents the effective velocity with which the electron drifts along x. It is an average velocity for one electron over many collisions, that is, over a long time (hence, $\Delta t \gg \tau$), so $\Delta x/\Delta t$ is a time average. Provided that Δt contains many collisions, it is reasonable to expect that the drift velocity $\Delta x/\Delta t$ from the time average for one electron is the same as the drift velocity v_{dx} per electron from averaging for all electrons at one instant, as in Equation 2.1, or

Drift velocity

$$\frac{\Delta x}{\Delta t} = v_{dx}$$

The two velocities are the same only under steady-state conditions ($\Delta t \gg \tau$). Example 2.4 derives v_{dx} for one electron and shows that it is the same as Equation 2.3.

EXAMPLE 2.1

PROBABILITY OF SCATTERING PER UNIT TIME AND THE MEAN FREE TIME If $1/\tau$ is defined as the mean probability per unit time that an electron is scattered, show that the mean time between collisions is τ.

SOLUTION

Consider an infinitesimally small time interval dt at time t. Let N be the number of unscattered electrons at time t. The probability of scattering during dt is $(1/\tau)\ dt$, and the number of scattered electrons during dt is $N(1/\tau)\ dt$. The change dN in N is thus

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

The negative sign indicates a reduction in N because, as electrons become scattered, N decreases. Integrating this equation, we can find N at any time t, given that at time $t = 0$, N_0 is the total number of unscattered electrons. Therefore,

Unscattered electron concentration

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

This equation represents the number of unscattered electrons at time t. It reflects an exponential decay law for the number of unscattered electrons. The above equation is called the probability distribution function for unscattered electrons in time. It is a probability distribution for free times.

The **mean free time** $\bar{t}$ can be calculated from the mathematical definition of $\bar{t}$,

Mean free time

$$\bar{t} = \frac{\int_0^\infty tN\,dt}{\int_0^\infty N\,dt} = \tau$$

where we have used $N = N_0\exp(-t/\tau)$. Clearly, $1/\tau$ is the **mean probability of scattering per unit time.**

It is left as an exercise to show that the exponential probability distribution of free times above can also be used to calculate the mean square time $\bar{t}^2$, which is $2\tau^2$.

EXAMPLE 2.2

ELECTRON DRIFT MOBILITY IN METALS Calculate the drift mobility and the mean scattering time of conduction electrons in copper at room temperature, given that the conductivity of copper is $5.9 \times 10^5\ \Omega^{-1}\ \text{cm}^{-1}$. The density of copper is 8.96 g cm^{-3} and its atomic mass is 63.5 g mol^{-1}. If the mean speed of the conduction electrons in Cu is roughly 1.6×10^6 m s^{-1}, what is the mean free path between collisions?

SOLUTION

We can calculate μ_d from $\sigma = en\mu_d$ because we already know the conductivity σ. The number of free electrons n per unit volume can be taken as equal to the number of Cu atoms per unit volume, if we assume that each Cu atom donates one electron to the conduction electron gas in the metal. One mole of copper has N_A (6.02×10^{23}) atoms and a mass of 63.5 g. Therefore, the number of copper atoms per unit volume is

$$n = \frac{dN_A}{M_{\text{at}}}$$

where d = density = 8.96 g cm^{-3}, and M_{at} = atomic mass = 63.5 (g mol^{-1}). Substituting for d, N_A, and M_{at}, we find $n = 8.5 \times 10^{22}$ electrons cm^{-3}.

The electron drift mobility is therefore

$$\mu_d = \frac{\sigma}{en} = \frac{5.9 \times 10^5\ \Omega^{-1}\ \text{cm}^{-1}}{[(1.6 \times 10^{-19}\ \text{C})(8.5 \times 10^{22}\ \text{cm}^{-3})]}$$
$$= 43.4\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$$

From the drift mobility we can calculate the mean free time τ between collisions by using Equation 2.5,

$$\tau = \frac{\mu_d m_e}{e} = \frac{(43.4 \times 10^{-4}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1})(9.1 \times 10^{-31}\ \text{kg})}{1.6 \times 10^{-19}\ \text{C}} = 2.5 \times 10^{-14}\ \text{s}$$

The mean speed u of the conduction electrons is about 1.6×10^6 m s^{-1}, so that their mean free path $\ell = u\tau = 39$ nm.

EXAMPLE 2.3 **DRIFT VELOCITY AND MEAN SPEED** What is the applied electric field that will impose a drift velocity equal to 0.1 percent of the mean speed u ($\sim 10^6$ m s^{-1}) of conduction electrons in copper? What is the corresponding current density and current through a Cu wire of diameter 1 mm?

SOLUTION

The drift velocity of the conduction electrons is $v_{dx} = \mu_d E_x$, where μ_d is the drift mobility, which for copper is 43.4 cm^2 V^{-1} s^{-1} (see Example 2.2). With $v_{dx} = 0.001u = 10^3$ m s^{-1}, we have

$$E_x = \frac{v_{dx}}{\mu_d} = \frac{10^3\ \text{m s}^{-1}}{43.4 \times 10^{-4}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}} = 2.3 \times 10^5\ \text{V m}^{-1} \quad \text{or} \quad 2.3\ \text{kV cm}^{-1}$$

This is an unattainably large electric field in a metal. Given the conductivity σ of copper, the equivalent current density is

$$J_x = \sigma E_x = (5.9 \times 10^7\ \Omega^{-1}\ \text{m}^{-1})(2.3 \times 10^5\ \text{V m}^{-1})$$
$$= 1.4 \times 10^{13}\ \text{A m}^{-2} \quad \text{or} \quad 1.4 \times 10^7\ \text{A mm}^{-2}$$

This means a current of 1.1×10^7 A through a 1 mm diameter wire! It is clear from this example that for all practical purposes, even under the highest working currents and voltages, the drift velocity is much smaller than the mean speed of the electrons. Consequently, when an electric field is applied to a conductor, for all practical purposes, the mean speed is unaffected.

EXAMPLE 2.4 **DRIFT VELOCITY IN A FIELD: A CLOSER LOOK** There is another way to explain the observed dependence of the drift velocity on the field, and Equation 2.3. Consider the path of a conduction electron in an applied field E_x as shown in Figure 2.4. Suppose that at time $t = 0$ the electron has just been scattered from a lattice vibration. Let u_{x1} be the initial velocity in the x direction just after this initial collision (to which we assign a collision number of zero). We will assume that immediately after a collision, the velocity of the electron is in a random *direction*. Suppose that the first collision occurs at time t_1. Since eE_x/m_e is the acceleration, the distance s_1 covered in the x direction during the free time t_1 will be

Distance traversed along x before collision

$$s_1 = u_{x1}t_1 + \frac{1}{2}\left(\frac{eE_x}{m_e}\right)t_1^2$$

At time t_1, the electron collides with a lattice vibration (its first collision), and the velocity is randomized again to become u_{x2}. The whole process is then repeated during the next

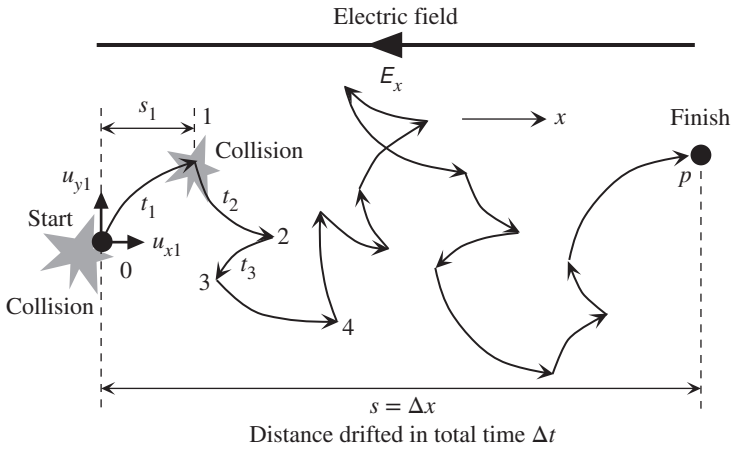


Figure 2.4 The motion of a single electron in the presence of an electric field E. During a time interval t_i, the electron traverses a distance s_i along x. After p collisions, it has drifted a distance $s = \Delta x$.

interval which lasts for a free time t_2, and the electron traverses a distance s_2 along x, and so on. To find the overall distance traversed by the electron after p such scattering events, we sum all the above distances s_1, s_2, . . . for p free time intervals,

$$s = s_1 + s_2 + \cdots + s_p = [u_{x1}t_1 + u_{x2}t_2 + \cdots + u_{xp}t_p] + \frac{1}{2}\left(\frac{eE_x}{m_e}\right)[t_1^2 + t_1^2 + \cdots + t_p^2] \qquad [2.8]$$

Since after a collision the "initial" velocity u_x is always random, the first term has u_x values that are randomly negative and positive, so for many collisions (large p) the first term on the right-hand side of Equation 2.8 is nearly zero and can certainly be neglected compared with the second term. Thus, after many collisions, the net distance $s = \Delta x$ traversed in the x direction is given by the second term in Equation 2.8, which is the electric field induced displacement term. If $\overline{t^2}$ is the **mean square free time,** then

Distance drifted after p scattering events

$$s = \frac{1}{2}\left(\frac{eE_x}{m_e}\right)p\overline{t^2}$$

where

$$\overline{t^2} = \frac{1}{p}[t_1^2 + t_1^2 + \cdots + t_p^2]$$

Mean square free time definition

Suppose that τ is the **mean free time between collisions,** where $\tau = (t_1 + t_2 + \cdots + t_p)/p$. We know from Example 2.1 that the probability that the electron will not be scattered, that is it is still free, decreases exponentially with time in which the mean free time $\bar{t}$ is τ. Using the same probability distribution function, we easily can show that $\overline{t^2} = 2(\bar{t})^2 = 2\tau^2$. So in terms of the mean free time τ between collisions, the overall distance $s = \Delta x$ drifted in the x direction after p collisions is

$$s = \frac{eE_x}{m_e}(p\tau^2)$$

Further, since the total time Δt taken for these p scattering events is simply $p\tau$, the drift velocity v_{dx} is given by $\Delta x/\Delta t$ or $s/(p\tau)$, that is,

$$v_{dx} = \frac{e\tau}{m_e}E_x \qquad [2.9]$$

Drift velocity and mean free time

[3] See Question 2.4 for the derivation.

This is the same expression as Equation 2.3, except that τ is defined here as the average free time for a single electron over a long time, that is, over many collisions, whereas previously it was the mean free time averaged over many electrons. Further, in Equation 2.9 v_{dx} is an average drift for an electron over a long time, over many collisions. In Equation 2.1 v_{dx} is the average velocity averaged over all electrons at one instant. For all practical purposes, the two are equivalent. (The equivalence breaks down when we are interested in events over a time scale that is comparable to one scattering, $\sim 10^{-14}$ second.)

The drift mobility μ_d from Equation 2.9 is identical to that of Equation 2.5, $\mu_d = e\tau/m_e$. Suppose that the mean speed of the electrons (not the drift velocity) is u. Then an electron moves a distance $\ell = u\tau$ in mean free time τ, which is called the **mean free path.** The drift mobility and conductivity become,

Drift mobility and conductivity and mean free path

$$\mu_d = \frac{e\ell}{m_e u} \quad \text{and} \quad \sigma = en\mu_d = \frac{e^2 n\ell}{m_e u} \qquad [2.10]$$

Equations 2.3 and 2.10 both assume that after each collision the velocity is randomized. The scattering process, lattice scattering, is able to randomize the velocity in one single scattering. In general not all electron scattering processes can randomize the velocity in one scattering process. If it takes more than one collision to randomize the velocity, then the electron is able to carry with it some velocity gained from a previous collision and hence possesses a higher drift mobility. In such cases one needs to consider the effective mean free path a carrier has to move to eventually randomize the velocity gained; this is a point considered in Chapter 4 when we calculate the resistivity at low temperatures.

2.2 TEMPERATURE DEPENDENCE OF RESISTIVITY: IDEAL PURE METALS

When the conduction electrons are only scattered by thermal vibrations of the metal ions, then τ in the mobility expression $\mu_d = e\tau/m_e$ refers to the mean time between scattering events by this process. The resulting conductivity and resistivity are denoted by σ_T and ρ_T, where the subscript T represents "thermal vibration scattering."

To find the temperature dependence of σ, we first consider the temperature dependence of the mean free time τ, since this determines the drift mobility. An electron moving with a mean speed u is scattered when its path crosses the cross-sectional area S of a scattering center, as depicted in Figure 2.5. The scattering

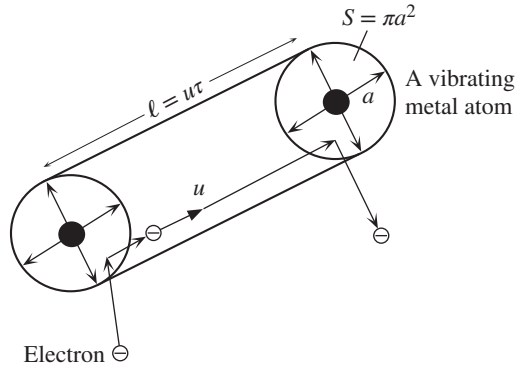


Figure 2.5 Scattering of an electron from the thermal vibrations of the atoms.

The electron travels a mean distance $\ell = u\tau$ between collisions. Since the scattering cross-sectional area is S, in the volume $S\ell$ there must be at least one scatterer, $N_s(Su\tau) = 1$.

center may be a vibrating atom, impurity, vacancy, or some other crystal defect. Since τ is the mean time taken for one scattering process, the **mean free path** ℓ of the electron between scattering processes is $u\tau$. If N_s is the concentration of scattering centers, then in the volume $S\ell$, there is one scattering center, that is, $(Su\tau)N_s = 1$. Thus, the mean free time is given by

Mean free time between collisions

$$\tau = \frac{1}{SuN_s} \qquad [2.11]$$

The mean speed u of conduction electrons in a metal can be shown to be only slightly temperature dependent.[4] In fact, electrons wander randomly around in the metal crystal with an almost constant mean speed that depends largely on their concentration and hence on the crystal material. Taking the number of scattering centers per unit volume to be the atomic concentration, the temperature dependence of τ then arises essentially from that of the cross-sectional area S. Consider what a free electron "sees" as it approaches a vibrating crystal atom as in Figure 2.5. Because the atomic vibrations are random, the atom covers a cross-sectional area πa^2, where a is the amplitude of the vibrations. If the electron's path crosses πa^2, it gets scattered. Therefore, the mean time between scattering events τ is inversely proportional to the area πa^2 that scatters the electron, that is, $\tau \propto 1/\pi a^2$.

The thermal vibrations of the atom can be considered to be simple harmonic motion, much the same way as that of a mass M attached to a spring. The average kinetic energy of the oscillations is $\frac{1}{4}Ma^2\omega^2$, where ω is the oscillation frequency. From the kinetic theory of matter, this average kinetic energy must be on the order of $\frac{1}{2}kT$. Therefore,

$$\frac{1}{4}Ma^2\omega^2 \approx \frac{1}{2}kT$$

so $a^2 \propto T$. Intuitively, this is correct because raising the temperature increases the amplitude of the atomic vibrations. Thus,

$$\tau \propto \frac{1}{\pi a^2} \propto \frac{1}{T} \qquad \text{or} \qquad \tau = \frac{C}{T}$$

where C is a temperature-independent constant. Substituting for τ in $\mu_d = e\tau/m_e$, we obtain

$$\mu_d = \frac{eC}{m_e T}$$

So, the resistivity ρ_T of a pure metal is

$$\rho_T = \frac{1}{\sigma_T} = \frac{1}{en\mu_d} = \frac{m_e T}{e^2 nC}$$

[4] The fact that the mean speed of electrons in a metal is only weakly temperature dependent can be proved from what it called the Fermi–Dirac statistics for the collection of electrons in a metal (as in Chapter 4). This result contrasts sharply with the kinetic molecular theory of gases (Chapter 1), which predicts that the mean speed of molecules is proportional to $\sqrt{T}$. For the time being, we simply use a constant mean speed u for the conduction electrons in a metal.

Pure metal resistivity due to thermal vibrations of the crystal

that is,

$$\rho_T = AT \qquad [2.12]$$

where A is a temperature-independent constant. This shows that the resistivity of a pure metal wire increases linearly with the temperature, and that the resistivity is due simply to the scattering of conduction electrons by the thermal vibrations of the atoms. We term this conductivity **lattice-scattering-limited conductivity.**[5]

EXAMPLE 2.5 **TEMPERATURE DEPENDENCE OF RESISTIVITY** What is the percentage change in the resistance of a pure metal wire from Saskatchewan's summer to winter, neglecting the changes in the dimensions of the wire?

SOLUTION

Assuming 20 °C for the summer and perhaps −30 °C for the winter, from $R \propto \rho = AT$, we have

$$\frac{R_{\text{summer}} - R_{\text{winter}}}{R_{\text{summer}}} = \frac{T_{\text{summer}} - T_{\text{winter}}}{T_{\text{summer}}} = \frac{(20 + 273) - (-30 + 273)}{(20 + 273)}$$
$$= 0.171 \quad \text{or} \quad 17\%$$

Notice that we have used the absolute temperature for T. How will the outdoor cable power losses be affected?

EXAMPLE 2.6 **DRIFT MOBILITY AND RESISTIVITY DUE TO LATTICE VIBRATIONS** Given that the mean speed of conduction electrons in copper is 1.6×10^6 m s^{-1} and the frequency of vibration of the copper atoms at room temperature is about 4×10^{12} s^{-1}, estimate the drift mobility of electrons and the conductivity of copper. The density d of copper is 8.96 g cm^{-3} and the atomic mass M_{at} is 63.56 g mol^{-1}.

SOLUTION

The method for calculating the drift mobility and hence the conductivity is based on evaluating the mean free time τ via Equation 2.11, that is, $\tau = 1/SuN_s$. Since τ is due to scattering from atomic vibrations, N_s is the atomic concentration,

$$N_s = \frac{dN_A}{M_{\text{at}}} = \frac{(8.96 \times 10^3 \text{ kg m}^{-3})(6.02 \times 10^{23} \text{ mol}^{-1})}{63.56 \times 10^{-3} \text{ kg mol}^{-1}}$$
$$= 8.5 \times 10^{28} \text{ m}^{-3}$$

The cross-sectional area $S = \pi a^2$ depends on the amplitude a of the thermal vibrations as shown in Figure 2.5. The average kinetic energy KE_{av} associated with a vibrating mass M attached to a spring is given by $KE_{\text{av}} = \frac{1}{4}Ma^2\omega^2$, where ω is the angular frequency of the vibration ($\omega = 2\pi 4 \times 10^{12}$ rad s^{-1}). Applying this equation to the vibrating atom and equating the average kinetic energy KE_{av} to $\frac{1}{2}kT$, by virtue of equipartition of energy theorem, we have $a^2 = 2kT/M\omega^2$ and thus

$$S = \pi a^2 = \frac{2\pi kT}{M\omega^2} = \frac{2\pi(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}{\left(\dfrac{63.56 \times 10^{-3} \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}\right)(2\pi \times 4 \times 10^{12} \text{ rad s}^{-1})^2}$$
$$= 3.9 \times 10^{-22} \text{ m}^2$$

[5] As will be apparent in Chapter 4, the actual explanation in the modern theory of solids is based on the concept of "phonons," quanta of lattice waves in the crystal, and how their concentration depends on the temperature.

Therefore,

$$\tau = \frac{1}{SuN_s} = \frac{1}{(3.9 \times 10^{-22}\ \text{m}^2)(1.6 \times 10^{6}\ \text{m s}^{-1})(8.5 \times 10^{28}\ \text{m}^{-3})}$$
$$= 1.9 \times 10^{-14}\ \text{s}$$

The drift mobility is

$$\mu_d = \frac{e\tau}{m_e} = \frac{(1.6 \times 10^{-19}\ \text{C})(1.9 \times 10^{-14}\ \text{s})}{(9.1 \times 10^{-31}\ \text{kg})}$$
$$= 3.3 \times 10^{-3}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1} = 33\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$$

The conductivity is then

$$\sigma = en\mu_d = (1.6 \times 10^{-19}\ \text{C})(8.5 \times 10^{22}\ \text{cm}^{-3})(33\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1})$$
$$= 4.5 \times 10^{5}\ \Omega^{-1}\ \text{cm}^{-1}$$

The experimentally measured value for the conductivity is $5.9 \times 10^5\ \Omega^{-1}\ \text{cm}^{-1}$, so our crude calculation based on Equation 2.11 is actually only 24 percent lower, which is not bad for a crude estimate. (As one might have surmised, the agreement is brought about by using reasonable values for the mean speed u and the atomic vibrational frequency ω. These values were taken from quantum mechanical calculations, so our evaluation for τ was not truly based on classical concepts.)

2.3 MATTHIESSEN'S AND NORDHEIM'S RULES

2.3.1 MATTHIESSEN'S RULE AND THE TEMPERATURE COEFFICIENT OF RESISTIVITY (α)

The theory of conduction that considers scattering from lattice vibrations only works well with pure metals; unfortunately, it fails for metallic alloys. Their resistivities are only weakly temperature dependent. We must therefore search for a different type of scattering mechanism.

Consider a metal alloy that has randomly distributed impurity atoms. An electron can now be scattered by the impurity atoms because they are not identical to the host atoms, as illustrated in Figure 2.6. The impurity atom need not be larger than the host atom; it can be smaller. As long as the impurity atom results in a local distortion of the crystal lattice, it will be effective in scattering. One way of looking at the scattering process from an impurity is to consider the scattering cross section. What actually scatters the electron is a local, unexpected change in the potential energy PE of the electron as it approaches the impurity, because the force experienced by the electron is given by

$$F = -\frac{d(PE)}{dx}$$

For example, when an impurity atom of a different size compared to the host atom is placed into the crystal lattice, the impurity atom distorts the region around it, either by pushing the host atoms farther away, or by pulling them in, as depicted in Figure 2.6. The cross section that scatters the electron is the lattice region that has

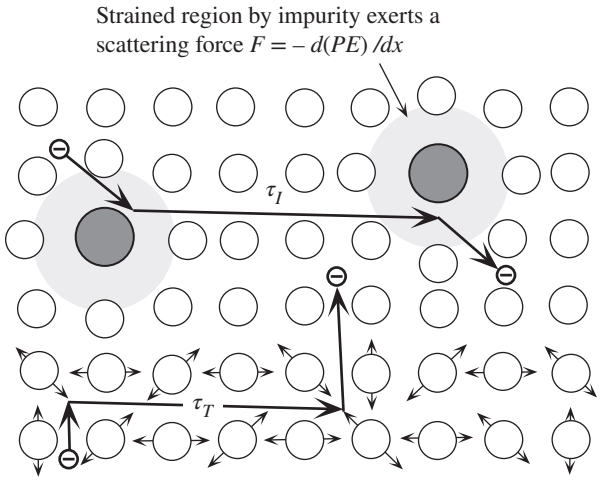


Figure 2.6 Two different types of scattering processes involving scattering from impurities alone and from thermal vibrations alone.

been elastically distorted by the impurity (the impurity atom itself and its neighboring host atoms), so that in this zone, the electron suddenly experiences a force $F = -d(PE)/dx$ due to a sudden change in the PE. This region has a large scattering cross section, since the distortion induced by the impurity may extend a number of atomic distances. These impurity atoms will therefore hinder the motion of the electrons, thereby increasing the resistance.

We now effectively have two types of mean free times between collisions: one, τ_T, for scattering from thermal vibrations only, and the other, τ_I, for scattering from impurities only. We define τ_T as the mean time between scattering events arising from thermal vibrations alone and τ_I as the mean time between scattering events arising from collisions with impurities alone. Both are illustrated in Figure 2.6.

In general, an electron may be scattered by both processes, so the effective mean free time τ between any two scattering events will be less than the individual scattering times τ_T and τ_I. The electron will therefore be scattered when it collides with either an atomic vibration or an impurity atom. Since in unit time, $1/\tau$ is the net probability of scattering, $1/\tau_T$ is the probability of scattering from lattice vibrations alone, and $1/\tau_I$ is the probability of scattering from impurities alone, then within the realm of elementary probability theory for independent events, we have

Overall frequency of scattering

$$\frac{1}{\tau} = \frac{1}{\tau_T} + \frac{1}{\tau_I} \qquad [2.13]$$

In writing Equation 2.13 for the various probabilities, we make the reasonable assumption that, to a greater extent, the two scattering mechanisms are essentially independent. Here, the effective mean scattering time τ is clearly smaller than both τ_T and τ_I. We can also interpret Equation 2.13 as follows: In unit time, the overall number of collisions $(1/\tau)$ is the sum of the number of collisions with thermal vibrations alone $(1/\tau_T)$ and the number of collisions with impurities alone $(1/\tau_I)$.

The drift mobility μ_d depends on the effective scattering time τ via $\mu_d = e\tau/m_e$, so Equation 2.13 can also be written in terms of the drift mobilities determined by

the various scattering mechanisms. In other words,

$$\frac{1}{\mu_d} = \frac{1}{\mu_L} + \frac{1}{\mu_I} \qquad [2.14]$$

Effective drift mobility

where μ_L is the **lattice-scattering-limited drift mobility,** and μ_I is the **impurity-scattering-limited drift mobility.** By definition, $\mu_L = e\tau_T/m_e$ and $\mu_I = e\tau_I/m_e$. The effective (or overall) resistivity ρ of the material is simply $1/en\mu_d$, or

$$\rho = \frac{1}{en\mu_d} = \frac{1}{en\mu_L} + \frac{1}{en\mu_I}$$

which can be written

$$\rho = \rho_T + \rho_I \qquad [2.15]$$

Matthiessen's rule

where $1/en\mu_L$ is defined as the resistivity due to scattering from thermal vibrations, and $1/en\mu_I$ is the resistivity due to scattering from impurities, or

Resistivities due to lattice and impurity scattering

$$\rho_T = \frac{1}{en\mu_L} \qquad \text{and} \qquad \rho_I = \frac{1}{en\mu_I}$$

The final result in Equation 2.15 simply states that the effective resistivity ρ is the sum of two contributions. First, $\rho_T = 1/en\mu_L$ is the resistivity due to scattering by thermal vibrations of the host atoms. For those near-perfect pure metal crystals, this is the dominating contribution. As soon as we add impurities, however, there is an additional resistivity, $\rho_I = 1/en\mu_I$, which arises from the scattering of the electrons from the impurities. The first term is temperature dependent because $\tau_T \propto T^{-1}$ (see Section 2.2), but the second term is not.

The mean time τ_I between scattering events involving electron collisions with impurity atoms depends on the separation between the impurity atoms and therefore on the concentration of those atoms (see Figure 2.6). If ℓ_I is the mean separation between the impurities, then the mean free time between collisions with impurities alone will be ℓ_I/u, which is temperature independent because ℓ_I is determined by the impurity concentration N_I (*i.e.*, $\ell_I = N_I^{-1/3}$), and the mean speed u of the electrons is nearly constant in a metal. In the absence of impurities, τ_I is infinitely long, and thus $\rho_I = 0$. The summation rule of resistivities from different scattering mechanisms, as shown by Equation 2.15, is called **Matthiessen's rule.**[6]

There may also be electrons scattering from dislocations and other crystal defects, as well as from grain boundaries. All of these scattering processes add to the resistivity of a metal, just as the scattering process from impurities. We can therefore write the effective resistivity of a metal as

$$\rho = \rho_T + \rho_R \qquad [2.16]$$

Matthiessen's rule

[6] The summation rule of resistivities in Equations 2.15 or 2.16 was discovered by Augustus Matthiessens (1831–1870), and reported in his experimental papers on the conductivity of metals and their alloys, published mainly in the Philosophical Transactions of the Royal Society of London, around 1857–1864. At the time it was not, of course, known as Matthiessen's rule and the rule itself is actually a modern conceptualization of his observations long after his papers. Matthiessen received the Royal Medal from the Royal Society in 1869 for his research on metals and alloys. There is an excellent discussion of Matthiessen's works by Simon Reif-Acherman in the *Proc. IEEE, 103,* 713, 2015.

where ρ_R is called the **residual resistivity** and is due to the scattering of electrons by impurities, dislocations, interstitial atoms, vacancies, grain boundaries, etc. (which means that ρ_R also includes ρ_I). The residual resistivity shows very little temperature dependence, whereas $\rho_T = AT$, so the effective resistivity ρ is given by

$$\rho \approx AT + B \tag{2.17}$$

where A and B are temperature-independent constants.

Equation 2.17 indicates that the resistivity of a metal varies almost linearly with the temperature, with A and B depending on the material. Instead of listing A and B in resistivity tables, we prefer to use a temperature coefficient that refers to small, normalized changes around a reference temperature. The **temperature coefficient of resistivity (TCR)** α_0 is defined as the fractional change in the resistivity per unit temperature increase at the reference temperature T_0, that is,

Definition of temperature coefficient of resistivity

$$\alpha_0 = \frac{1}{\rho_0}\left[\frac{\delta\rho}{\delta T}\right]_{T=T_0} \tag{2.18}$$

where ρ_0 is the resistivity at the reference temperature T_0, usually 273 K (0 °C) or 293 K (20 °C), and $\delta\rho = \rho - \rho_0$ is the change in the resistivity due to a small increase in temperature, $\delta T = T - T_0$.

When the resistivity follows the behavior $\rho \approx AT + B$ in Equation 2.17, then according to Equation 2.18, α_0 is constant over a temperature range T_0 to T, and Equation 2.18 leads to the well-known equation,

Temperature dependence of resistivity

$$\rho = \rho_0[1 + \alpha_0(T - T_0)] \tag{2.19}$$

Equation 2.19 is actually only valid when α_0 is constant over the temperature range of interest, which requires Equation 2.17 to hold. Over a limited temperature range, this will usually be the case. Although it is not obvious from Equation 2.19, we should note that α_0 depends on the reference temperature T_0, by virtue of ρ_0 depending on T_0.

The equation $\rho = AT$, which we used for pure-metal crystals to find the change in the resistance with temperature, is only approximate; nonetheless, for pure metals, it is useful to recall in the absence of tabulated data. To determine how good the formula $\rho = AT$ is, put it in Equation 2.19, which leads to $\alpha_0 = T_0^{-1}$. If we take the reference temperature T_0 as 273 K (0 °C), then α_0 is simply $1/273$ K; stated differently, Equation 2.19 is then equivalent to $\rho = AT$.

Table 2.1 shows that $\rho \propto T$ is not a bad approximation for some of the familiar pure metals used as conductors (Cu, Al, Au, etc.), but it fails badly for others, in particular, the magnetic metals such as iron and nickel.

The temperature dependence of the resistivity of various metals is shown in Figure 2.7, where it is apparent that except for the magnetic materials, the linear relationship $\rho \propto T$ seems to be approximately obeyed almost all the way to the melting temperature for many pure metals. It should also be noted that for the alloys, such as nichrome (Ni–Cr), the resistivity is essentially dominated by the residual resistivity, so the resistivity is relatively temperature insensitive, with a very small TCR.

Table 2.1 Resistivity and thermal coefficient of resistivity α_0 at 273 K (0 °C) for various pure metals above 200 K but below their melting temperatures. The resistivity index n in $\rho \propto T^n$ is also shown.

Metal	ρ_0(nΩ m)	$\alpha_0(1/K)$	n	Range and Comment
Aluminum, Al	24.2	$\frac{1}{227}$	1.20	200–800 K
Antimony	390	$\frac{1}{215}$	1.27	80–400 K
Copper, Cu	15.4	$\frac{1}{233}$	1.16	200–1100 K
Gold, Au	20.5	$\frac{1}{242}$	1.13	225–1000 K
Indium, In	80	$\frac{1}{208}$	1.31	200–400 K
Molybdenum, Mo	48.5	$\frac{1}{226}$	1.21	200–2400 K
Platinum, Pt	98.1	$\frac{1}{256}$	1.01	200–1273 K
Silver, Ag	14.7	$\frac{1}{242}$	1.13	200–1100 K
Strontium, Sr	123	$\frac{1}{276}$	0.99	273–800 K
Tin, Sn	115	$\frac{1}{248}$	1.10	200–490 K
Tungsten, W	48.2	$\frac{1}{210}$	1.24	200–3000 K
Iron, Fe	85.7	$\frac{1}{159}$	1.73	200–900 K; magnetic
Nickel, Ni	61.6	$\frac{1}{155}$	1.76	200–700 K; magnetic

NOTE: $\rho \propto T^n$ fitted to data mainly from the Ed. Haynes, W.M., *CRC Handbook of Chemistry and Physics,* 96th Edition, 2015-2016, Boca Raton, FL: CRC Press and Kaye and Laby Tables of Physical and Chemical Tables at the National Physical Laboratory Website. The temperature range for the $\rho \propto T^n$ fit is also given. Ideally, at T_0, TCR, $\alpha_0 = n/T_0$.

Frequently, the resistivity versus temperature behavior of pure metals can be empirically represented by a power law of the form

Resistivity of pure metals

$$\rho = \rho_0 \left[\frac{T}{T_0}\right]^n \qquad [2.20]$$

where ρ_0 is the resistivity at the reference temperature T_0, and n is a characteristic index that best fits the data. Table 2.1 lists some typical n values for various pure metals above 0 °C. It is apparent that for the nonmagnetic metals, n is close to unity, whereas it is closer to 2 than 1 for the magnetic metals Fe and Ni. In iron, for example, the conduction electron is not scattered simply by atomic vibrations, as in

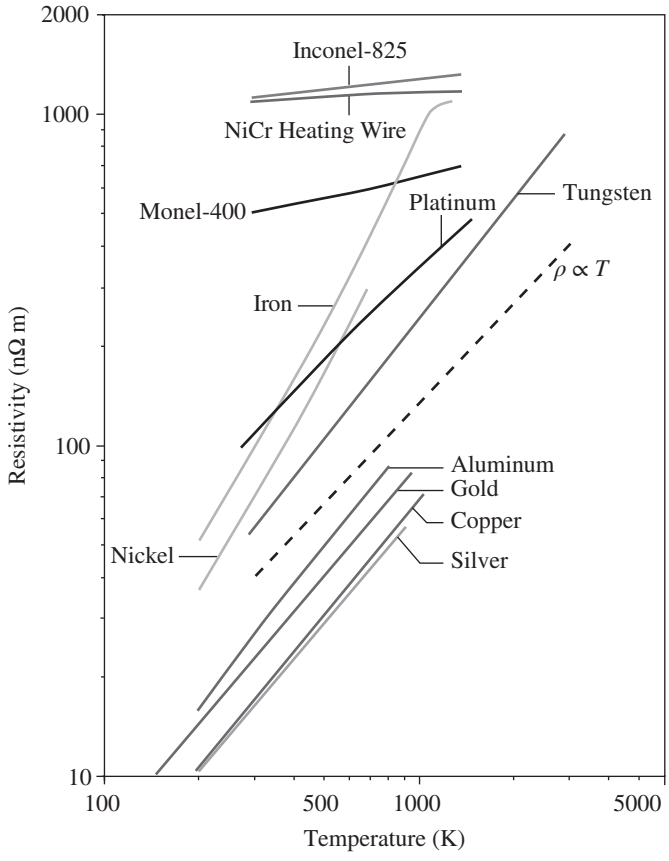


Figure 2.7 Nickel and iron go through a magnetic-to-nonmagnetic (Curie) transformation at about 627 K and 1043 K, respectively. The theoretical behavior ($\rho \propto T$) is shown for reference.

SOURCE: *Metals Handbook,* 10th ed., vol. 2 and 3, Metals Park, OH: ASM International, 1991, along with other sources.

copper, but is affected by its magnetic interaction with the Fe ions in the lattice. This leads to a complicated temperature dependence.

Although our oversimplified theoretical analysis predicts a linear $\rho = AT + B$ behavior for the resistivity down to the lowest temperatures, this is not true in reality, as depicted for copper in Figure 2.8. As the temperature decreases, typically below ~100 K for many metals, our simple and gross assumption that all the atoms are vibrating with a constant frequency fails. Indeed, the number of atoms that are vibrating with sufficient energy to scatter the conduction electrons starts to decrease rapidly with decreasing temperature, so the resistivity due to scattering from thermal vibrations becomes more strongly temperature dependent. The mean free time $\tau = 1/SuN_s$ becomes longer and strongly temperature dependent, leading to a smaller resistivity than the $\rho \propto T$ behavior. A full theoretical analysis, which is beyond the scope of this chapter, shows that $\rho \propto T^5$. Thus, at the lowest temperature, from

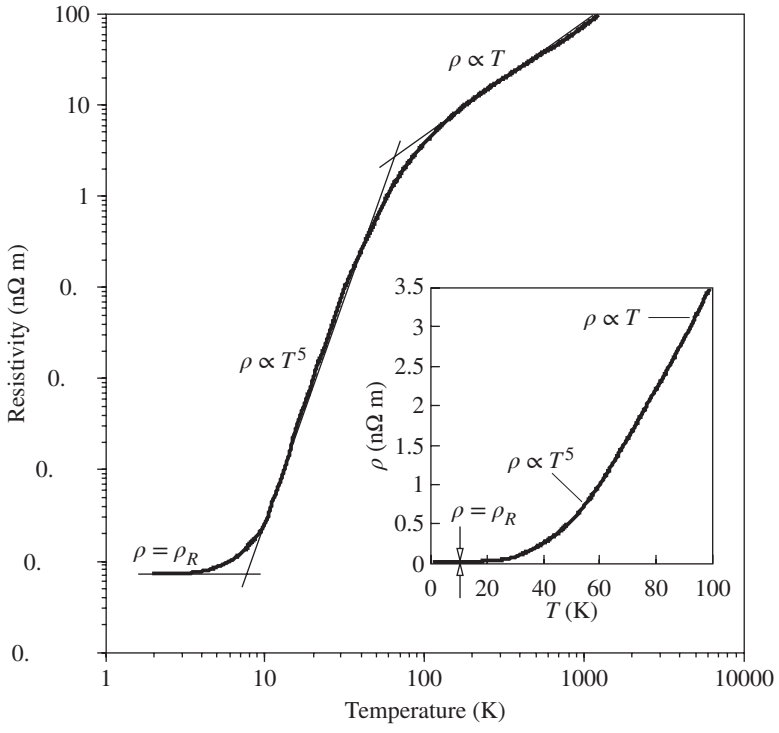


Figure 2.8 The resistivity of copper from lowest to highest temperatures (near melting temperature, 1358 K) on a log-log plot.

Above about 100 K, $\rho \propto T$, whereas at low temperatures, $\rho \propto T^5$, and at the lowest temperatures ρ approaches the residual resistivity ρ_R. The inset shows the ρ versus T behavior below 100 K on a linear plot. (ρ_R is too small on this scale.)

Matthiessen's rule, the resistivity becomes $\rho = DT^5 + \rho_R$, where D is a constant. Since the slope of ρ versus T is $d\rho/dT = 5DT^4$, which tends to zero as T becomes small, we have ρ curving toward ρ_R as T decreases toward 0 K. This is borne out by experiments, as shown in Figure 2.8 for copper. Therefore, at the lowest temperatures of interest, the resistivity is limited by scattering from impurities and crystal defects.[7]

EXAMPLE 2.7

MATTHIESSEN'S RULE Explain the typical resistivity versus temperature behavior of annealed and cold-worked (deformed) copper containing various amounts of Ni as shown in Figure 2.9.

SOLUTION

When small amounts of nickel are added to copper, the resistivity increases by virtue of Matthiessen's rule, $\rho = \rho_T + \rho_R + \rho_I$, where ρ_T is the resistivity due to scattering from thermal vibrations; ρ_R is the residual resistivity of the copper crystal due to scattering from crystal defects, dislocations, trace impurities, etc.; and ρ_I is the resistivity arising from Ni addition

[7] At sufficiently low temperatures (typically, below 10–20 K for many metals and below ~135 K for certain ceramics) certain materials exhibit superconductivity in which the resistivity vanishes ($\rho = 0$), even in the presence of impurities and crystal defects. Superconductivity and its quantum mechanical origin will be explained in Chapter 8.

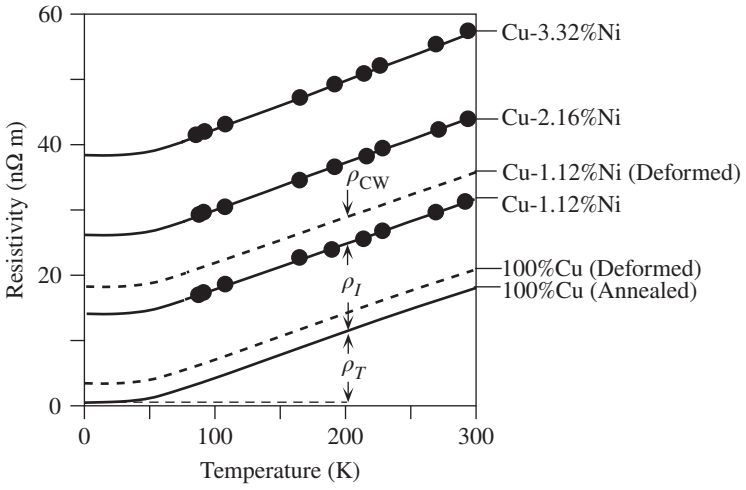


Figure 2.9 Typical temperature dependence of the resistivity of annealed and cold-worked (deformed) copper containing various amounts of Ni in atomic percentage.
SOURCE: Linde, J.O., *Annalen der Physik,* 5, 219, 1932.

alone (scattering from Ni impurity regions). Since ρ_I is temperature independent, for small amounts of Ni addition, ρ_I will simply shift up the ρ versus T curve for copper, by an amount proportional to the Ni content, $\rho_I \propto N_{\text{Ni}}$, where N_{Ni} is the Ni impurity concentration. This is apparent in Figure 2.9, where the resistivity of Cu–2.16% Ni is almost twice that of Cu–1.12% Ni. Cold working (CW) or deforming a metal results in a higher concentration of dislocations and therefore increases the residual resistivity ρ_R by ρ_{CW}. Thus, cold-worked samples have a resistivity curve that is shifted up by an additional amount ρ_{CW} that depends on the extent of cold working.

EXAMPLE 2.8 **TEMPERATURE COEFFICIENT OF RESISTIVITY α AND RESISTIVITY INDEX *n*** If α_0 is the temperature coefficient of resistivity (TCR) at temperature T_0 and the resistivity obeys the equation

$$\rho = \rho_0 \left[\frac{T}{T_0}\right]^n$$

show that

$$\alpha_0 = \frac{n}{T_0}\left[\frac{T}{T_0}\right]^{n-1}$$

What is your conclusion?

Experiments indicate that $n \approx 1.24$ for W. What is its α_0 at 20 °C? Given that, experimentally, $\alpha_0 = 0.00393\ \text{K}^{-1}$ for Cu at 20 °C, what is n?

SOLUTION

Since the resistivity obeys $\rho = \rho_0\,(T/T_0)^n$, we substitute this equation into the definition of TCR,

$$\alpha_0 = \frac{1}{\rho_0}\left[\frac{d\rho}{dT}\right] = \frac{n}{T_0}\left[\frac{T}{T_0}\right]^{n-1}$$

It is clear that, in general, α_0 depends on the temperature T, as well as on the reference temperature T_0. The TCR is only independent of T when $n = 1$, which leads to Equation 2.19.

At $T = T_0$, we have

$$\frac{\alpha_0 T_0}{n} = 1 \qquad \text{or} \qquad n = \alpha_0 T_0$$

For W, $n = 1.24$, so at $T = T_0 = 293$ K, we have $\alpha_{293\ \mathrm{K}} = 0.0041\ \mathrm{K}^{-1}$, which agrees reasonably well with $\alpha_{293\ \mathrm{K}} = 0.0044\ \mathrm{K}^{-1}$, frequently found in data books.

For Cu, $\alpha_{293\ \mathrm{K}} = 0.00393\ \mathrm{K}^{-1}$, so that $n = 1.15$, which is very close to the value of 1.16 in Table 2.1.

EXAMPLE 2.9

TCR AT DIFFERENT REFERENCE TEMPERATURES If α_1 is the temperature coefficient of resistivity (TCR) at temperature T_1 and α_0 is the TCR at T_0, show that

$$\alpha_1 = \frac{\alpha_0}{1 + \alpha_0(T_1 - T_0)}$$

SOLUTION

Consider the resistivity at temperature T in terms of α_0 and α_1:

$$\rho = \rho_0[1 + \alpha_0(T - T_0)] \qquad \text{and} \qquad \rho = \rho_1[1 + \alpha_1(T - T_1)]$$

These equations are expected to hold at any temperature T, so the first and second equations at T_1 and T_0, respectively, give

$$\rho_1 = \rho_0[1 + \alpha_0(T_1 - T_0)] \qquad \text{and} \qquad \rho_0 = \rho_1[1 + \alpha_1(T_0 - T_1)]$$

These two equations can be readily solved to eliminate ρ_0 and ρ_1 to obtain

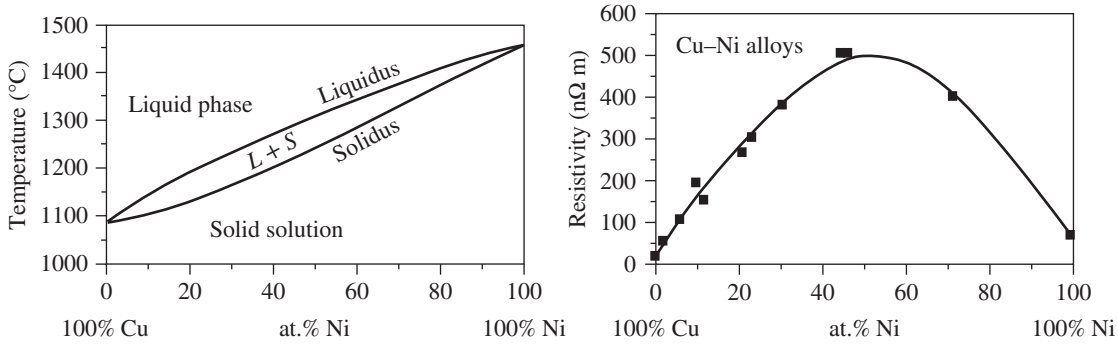
$$\alpha_1 = \frac{\alpha_0}{1 + \alpha_0(T_1 - T_0)}$$

2.3.2 SOLID SOLUTIONS AND NORDHEIM'S RULE

In an isomorphous alloy of two metals, that is, a binary alloy that forms a solid solution, we would expect Equation 2.15 to apply, with the temperature-independent impurity contribution ρ_I increasing with the concentration of solute atoms. This means that as the alloy concentration increases, the resistivity ρ increases and becomes less temperature dependent as ρ_I overwhelms ρ_T, leading to $\alpha \ll 1/273$. This is the advantage of alloys in resistive components. Table 2.2 shows that when 80% nickel is alloyed with 20% chromium, the resistivity of Ni increases almost 16 times, and there is a corresponding drop in α. In fact, the alloy is called **nichrome** and is widely used as a heater wire in household appliances and industrial furnaces.

Table 2.2 The effect of alloying on the resistivity

Material	Resistivity at 20 °C (nΩ m)	α at 20 °C (1/K)
Nickel	69	0.0064
Chrome	129	0.0030
Nichrome (80%N-20% Cr)	1100	0.0004



(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) The resistivity of the Cu–Ni alloy as a function of Ni content (at.%) at room temperature.

Figure 2.10 The Cu–Ni alloy system.
SOURCES: *Metals Handbook,* 10th ed., vol. 2 and 3, Metals Park, OH: ASM International, 1991 and Hansen, M. and Anderko, K., *Constitution of Binary Alloys,* New York, NY: McGraw-Hill, 1958.

As a further example of the resistivity of a solid solution, consider the copper–nickel alloy. The phase diagram for this alloy system is shown in Figure 2.10a. It is clear that the alloy forms a one-phase solid solution for all compositions. Both Cu and Ni have the same FCC crystal structure, and since the Cu atom is only slightly larger than the Ni atom by about ∼3 percent (easily checked on the Periodic Table), the Cu–Ni alloy will therefore still be FCC, but with Cu and Ni atoms randomly mixed, resulting in a solid solution. When Ni is added to copper, the impurity resistivity ρ_I in Equation 2.15 will increase with the Ni concentration. Experimental results for this alloy system are shown in Figure 2.10b. It should be apparent that when we reach 100% Ni, we again have a pure metal whose resistivity must be small. Therefore, ρ versus Ni concentration must pass through a maximum, which for the Cu–Ni alloy seems to be at around ∼50% Ni.

There are other binary solid solutions that reflect similar behavior to that depicted in Figure 2.10, such as Cu–Au, Ag–Au, Pt–Pd, Cu–Pd, to name a few. Quite often, the use of an alloy for a particular application is necessitated by the mechanical properties, rather than the desired electrical resistivity alone. For example, brass, which is 70% Cu–30% Zn in solid solution, has a higher strength compared to pure copper; as such, it is a suitable metal for the prongs of an electrical plug.

Nordheim's rule for solid solutions

An important semiempirical equation that can be used to predict the resistivity of an alloy is **Nordheim's rule** which relates the impurity resistivity ρ_I to the atomic fraction X of solute atoms in a solid solution, as follows:

$$\rho_I = CX(1 - X) \qquad [2.21]$$

where C is the constant termed the **Nordheim coefficient,** which represents the effectiveness of the solute atom in increasing the resistivity. Nordheim's rule assumes

that the solid solution has the solute atoms randomly distributed in the lattice, and these random distributions of impurities cause the electrons to become scattered as they whiz around the crystal. For sufficiently small amounts of impurity, experiments show that the increase in the resistivity ρ_I is nearly always simply proportional to the impurity concentration X, that is, $\rho_I \propto X$, which explains the initial approximately equal increments of rise in the resistivity of copper with 1.12% Ni and 2.16% Ni additions as shown in Figure 2.9. For dilute solutions, Nordheim's rule predicts the same linear behavior, that is, $\rho_I = CX$ for $X \ll 1$.

Table 2.3 lists some typical Nordheim coefficients for various additions to copper and gold. The value of the Nordheim coefficient depends on the type of solute and the solvent. A solute atom that is drastically different in size to the solvent atom will result in a bigger increase in ρ_I and will therefore lead to a larger C. An important assumption in Nordheim's rule in Equation 2.21 is that the alloying does not significantly vary the number of conduction electrons per atom in the alloy. Although this will be true for alloys with the same valency, that is, from the same column in the Periodic Table (*e.g.*, Cu–Au, Ag–Au), it will not be true for alloys of different valency, such as Cu and Zn. In pure copper, there is just one conduction electron per atom, whereas each Zn atom can donate two conduction electrons. As the Zn content in brass is increased, more conduction electrons become available per atom. Consequently, the resistivity predicted by Equation 2.21 at high Zn contents is greater than the actual value because C refers to dilute alloys. To get the correct resistivity from Equation 2.21 we have to lower C, which is equivalent to using an effective Nordheim coefficient C_{eff} that decreases as the Zn content increases. In other cases, for example, in Cu–Ni alloys, we have to increase C at high Ni concentrations to account for additional electron scattering mechanisms that develop with Ni addition.

Table 2.3 Nordheim coefficient C (at 20 °C) for dilute alloys obtained from $\rho_I = CX$ and $X < 1$ at.%

Solute in Solvent (element in matrix)	C (nΩ m)	Maximum Solubility at 25 °C (at.%)
Au in Cu matrix	5500	100
Mn in Cu matrix	2900	24
Ni in Cu matrix	1200	100
Sn in Cu matrix	2900	0.6
Zn in Cu matrix	300	30
Cu in Au matrix	450	100
Mn in Au matrix	2410	25
Ni in Au matrix	790	100
Sn in Au matrix	3360	5
Zn in Au matrix	950	15

NOTE: For many isomorphous alloys C may be different at higher concentrations; that is, it may depend on the composition of the alloy.

SOURCES: Fink, D.G., and Christiansen, D., eds., *Electronics Engineers' Handbook,* 2nd ed., New York, NY: McGraw-Hill, 1982. Stanley, J.K., *Electrical and Magnetic Properties of Metals,* American Society for Metals, Metals Park, OH, 1963. Hansen, M. and Anderko, K., *Constitution of Binary Alloys,* 2nd ed., McGraw-Hill, New York, NY, 1985.

Nonetheless, the Nordheim rule is still a very useful tool for predicting the resistivities of dilute alloys, particularly in the low-concentration region.

Combined Matthiessen and Nordheim rules

With Nordheim's rule in Equation 2.21, the resistivity of an alloy of composition X is

$$\rho = \rho_{\text{matrix}} + CX\,(1 - X) \qquad [2.22]$$

where $\rho_{\text{matrix}} = \rho_T + \rho_R$ is the resistivity of the matrix due to scattering from thermal vibrations and from other defects, in the absence of alloying elements. To reiterate, the value of C depends on the alloying element and the matrix. For example, C for gold in copper would be different than C for copper in gold, as shown in Table 2.3.

In solid solutions, at some concentrations of certain binary alloys, such as 75% Cu–25% Au and 50% Cu–50% Au, the annealed solid has an orderly structure; that is, the Cu and Au atoms are not randomly mixed, but occupy regular sites. In fact, these compositions can be viewed as pure compounds—like the solids Cu_3Au and CuAu. The resistivities of Cu_3Au and CuAu will therefore be less than the same composition random alloy that has been quenched from the melt. As a consequence, the resistivity ρ versus composition X curve does not follow the dashed parabolic curve throughout; rather, it exhibits sharp falls at these special compositions, as illustrated in Figure 2.11.

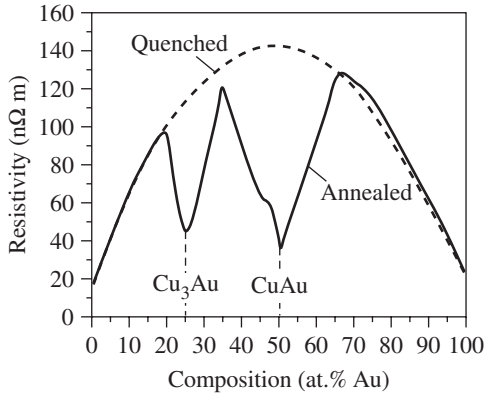
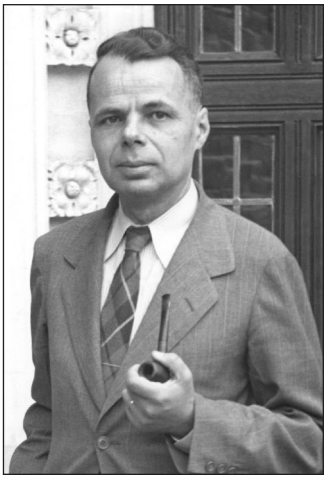


Figure 2.11 Electrical resistivity versus composition at room temperature in Cu–Au alloys. The quenched sample (dashed curve) is obtained by quenching the liquid, and the Cu and Au atoms are randomly mixed. The resistivity obeys the Nordheim rule. When the quenched sample is annealed or the liquid is 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.



Lothar Nordheim (1923–1985) was a German physicist who obtained his PhD from University of Göttingen. He immigrated to the USA in 1934, and later became a physics professor at Duke University. The Nordheim rule in this chapter for the increase in the resistivity of a solid solution with added solute atoms is based on his theoretical work published in Annalen der Physik in 1931. His name will come up again in Chapter 4 under the Fowler–Nordheim tunneling current at high electric fields.

| Courtesy of Duke University.

EXAMPLE 2.10

NORDHEIM'S RULE The alloy 90 wt.% Au–10 wt.% Cu is sometimes used in low-voltage dc electrical contacts, because pure gold is mechanically soft and the addition of copper increases the hardness of the metal without sacrificing the corrosion resistance. Predict the resistivity of the alloy and compare it with the experimental value of 108 nΩ m.

SOLUTION

We apply Equation 2.22, $\rho(X) = \rho_{Au} + CX(1 - X)$ but with 10 wt.% Cu converted to the atomic fraction for X. If w is the weight fraction of Cu, $w = 0.1$, and if M_{Au} and M_{Cu} are the atomic masses of Au and Cu, then the atomic fraction X of Cu is given by (see Example 1.2),

$$X = \frac{w/M_{Cu}}{w/M_{Cu} + (1 - w)/M_{Au}} = \frac{0.1/63.55}{(0.1/63.55) + (0.90/197)} = 0.256$$

Given that $\rho_{Au} = 22.8$ nΩ m and $C = 450$ nΩ m,

$$\rho = \rho_{Au} + CX(1 - X) = (22.8 \text{ n}\Omega \text{ m}) + (450 \text{ n}\Omega \text{ m})(0.256)(1 - 0.256)$$
$$= 108.5 \text{ n}\Omega \text{ m}$$

This value is only 0.5% different from the experimental value.

EXAMPLE 2.11

RESISTIVITY DUE TO IMPURITIES The mean speed of conduction electrons in copper is about 1.6×10^6 m s^{-1}. Its room temperature resistivity is 17 nΩ m, and the atomic concentration N_{at} in the crystal is 8.5×10^{22} cm^{-3}. Suppose that we add 1 at.% Au to form a solid solution. What is the resistivity of the alloy, the effective mean free path, and the mean free path due to collisions with Au atoms only?

SOLUTION

According to Table 2.3, the Nordheim coefficient C of Au in Cu is 5500 nΩ m. With $X = 0.01$ (1 at.%), the overall resistivity from Equation 2.22 is

$$\rho = \rho_{matrix} + CX(1 - X) = 17 \text{ n}\Omega \text{ m} + (5500 \text{ n}\Omega \text{ m})(0.01)(1 - 0.01)$$
$$= 17 \text{ n}\Omega \text{ m} + 54.45 \text{ n}\Omega \text{ m} = 71.45 \text{ n}\Omega \text{ m}$$

Suppose that ℓ is the overall or effective mean free path and τ is the effective mean free time between scattering events (includes both scattering from lattice vibrations and impurities). Since $\ell = u\tau$, and the effective drift mobility $\mu_d = e\tau/m_e$, the expression for the conductivity becomes

Conductivity and mean free path

$$\sigma = en\mu_d = \frac{e^2 n\tau}{m_e} = \frac{e^2 n\ell}{m_e u}$$

We can now calculate the effective mean free path ℓ in the alloy given that copper has a valency of 1 and the electron concentration $n = N_{at}$,

$$\frac{1}{71.5 \times 10^{-9} \ \Omega \text{ m}} = \frac{(1.6 \times 10^{-19} \text{ C})^2 (8.5 \times 10^{28} \text{ m}^{-3})\ell}{(9.1 \times 10^{-31} \text{ kg})(1.6 \times 10^6 \text{ m s}^{-1})}$$

which gives $\ell = 9.4$ nm. We can repeat the calculation for pure copper using $\sigma = 1/\rho_{matrix} = 1/(17 \times 10^{-9} \ \Omega \text{ m})$ to find $\ell_{Cu} = 39$ nm. The mean free path is reduced approximately by 4 times by adding only 1 at.% Au. The mean free path ℓ_I due to scattering from impurities only can be found from Equation 2.13 multiplied through by $1/u$, or by using Matthiessen's rule in Equation 2.14:

$$\frac{1}{\ell} = \frac{1}{\ell_{Cu}} + \frac{1}{\ell_I}$$

Substituting $\ell_{Cu} = 39$ nm and $\ell = 9.4$ nm, we find $\ell_I = 12.4$ nm.

We can take these calculations one step further. If N_I is the impurity concentration in the alloy, then $N_I = 0.01N_{at} = 0.01(8.5 \times 10^{28}\ \text{m}^{-3}) = 8.5 \times 10^{26}\ \text{m}^{-3}$. The mean separation d_I between the impurities can be estimated roughly from $d_I \approx 1/N_I^{1/3}$, which gives $d_I \approx 1.0$ nm. It is clear that not all Au atoms can be involved in scattering the electrons since ℓ_I is much longer than d_I. (Another way to look at it is to say that it takes more than just one collision with an impurity to randomize the velocity of the electron.)

EXAMPLE 2.12 **ALLOYS AND TCR** Using the resistivities of Ni and nichrome, the TCR of Ni in Table 2.2, and the combined Mathiessens and Nordheim rules, find the TCR of nichrome.

SOLUTION

For an alloy *AB* in which *A* is the solvent (matrix) and *B* is the solute (added atoms), Equation 2.22 is

$$\rho_{AB} = \rho_A + CX(1 - X)$$

TCR describes the change in ρ due to a change in T, so we differentiate the above equation with respect to T and assume that C is temperature independent

$$\frac{d\rho_{AB}}{dT} = \frac{d\rho_A}{dT}$$

so that the TCR of *AB* is

$$\alpha_{AB} = \frac{1}{\rho_{AB}}\left(\frac{d\rho_{AB}}{dT}\right) = \frac{1}{\rho_{AB}}\left(\frac{d\rho_A}{dT}\right) = \frac{\rho_A}{\rho_{AB}}\left(\frac{d\rho_A}{\rho_A dT}\right)$$

which gives

TCR for an alloy AB

$$\alpha_{AB} = \frac{\rho_A}{\rho_{AB}}\alpha_A \qquad [2.23]$$

Using the values from Table 2.2

$$\alpha_{AB} = \frac{(69\ \text{n}\Omega\ \text{m})}{(1100\ \text{n}\Omega\ \text{m})}(0.0064\ \text{K}^{-1}) = 0.00040\ \text{K}^{-1} \text{ or } 4.0 \times 10^{-4}\ \text{K}^{-1}$$

which is what is shown in Table 2.2 for nichrome. Equation 2.23 brings home the distinct advantage of alloys. Their TCR is much lower than the solvent metal.

EXAMPLE 2.13 **DESIGN OF STRAIN GAUGES** A **strain gauge** is a transducer attached to a body to measure its fractional elongation $\Delta L/L$, or the strain, under an applied load (force) F. The gauge is a grid of many folded runs of a thin, resistive wire glued to (or embedded in) a flexible backing, as depicted in Figure 2.12. (See also photo on page 211.) The gauge is bonded to the body under test such that the resistive wire length is parallel to the strain. Suppose that the strain does not change the resistivity ρ,[8] then the resistance R of the gauge wire is

$$R = \frac{\rho L}{\pi(D/2)^2} \qquad [2.24]$$

[8] For most metals, this is a good assumption but not for semiconductors in which there is a change in the resistivity with strain as explained in Chapter 5. By the way, both *gage* and *gauge* are used though many electrical engineers use *gage* with strain gages.

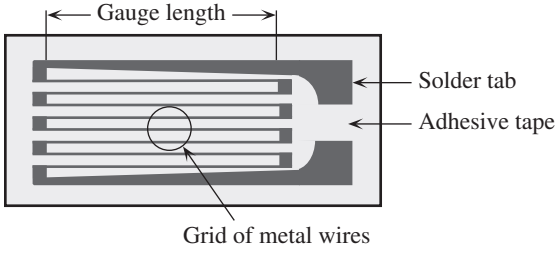


Figure 2.12 The strain gauge consists of a long thin wire folded several times along its length to form a grid as shown above and embedded in a self-adhesive tape. The ends of the wire are attached to terminals (solder pads) for external connections. The tape is stuck on the component whose strain is to be measured.

where L and D are the length and diameter of the wire, respectively. The applied load changes L and D by δL and δD, which change R by δR. The total derivative of a function R of two variables L and D can be found by taking partial differentials (like those used for error calculations in physics labs)

$$\delta R = \left(\frac{\partial R}{\partial L}\right)\delta L + \left(\frac{\partial R}{\partial D}\right)\delta D$$

so that we can substitute Equation 2.24 into the above equation, differentiate, and then divide by R to find

$$\frac{\delta R}{R} = \frac{\delta L}{L} - 2\frac{\delta D}{D} \qquad [2.25]$$

The longitudinal and transverse strains, ε_l and ε_t, are defined as follows:

$$\frac{\delta L}{L} = \varepsilon_l \qquad \text{and} \qquad \frac{\delta D}{D} = \varepsilon_t = -\nu\varepsilon_l$$

where ν is the Possion ratio (defined $\nu = \varepsilon_t/\varepsilon_l$). The strain we wish to measure is ε_l, or simply ε ($= \varepsilon_l$). We can substitute the above definitions into Equation 2.25 to derive the **metal strain gauge equation**

Metal strain gauge equation

$$\frac{\delta R}{R} = (1 + 2\nu)\varepsilon \qquad [2.26]$$

The **gauge factor** is an important gauge metric, defined as

Metal strain gauge factor

$$\text{GF} = \frac{\text{Fractional change in gauge property}}{\text{Input signal}} = \frac{\delta R/R}{\varepsilon} = 1 + 2\nu \qquad [2.27]$$

For many metals, $\nu \approx 1/3$, so that typically GF is roughly 1.67.

A major problem with strain gauges is that the change in R can be due to a change δT in temperature rather than strain ε. A change δT would increase L, D, and ρ. We can differentiate R with respect to T by considering that ρ, L, and D depend on T. If α is the temperature coefficient of resistivity and λ is the linear expansion coefficient, then differentiating Equation 2.23

Effect of temperature

$$\left(\frac{1}{R}\right)\frac{dR}{dT} = \alpha - \lambda \qquad [2.28]$$

Typically, $\lambda \approx 2 \times 10^{-5}$ K^{-1}, and for pure metals, from Table 2.1 that $\alpha \approx 1/273$ K^{-1} or 3.6×10^{-3} K^{-1}. A 1 °C fluctuation in the temperature will result in $\delta R/R = 3.6 \times 10^{-3}$, which is about the same as $\delta R/R$ from a strain of $\varepsilon = 2 \times 10^{-3}$ at a constant temperature. Clearly, temperature fluctuations would not allow sensible strain measurements if we were to use a

pure metal wire. Metal strain gauges therefore use alloys such as nichrome or constantan in which α is very small. Further, engineers use strain gauges in special resistance bridge configurations to further reduce the effects of temperature variations. (See Question 2.23.)

Even if we make $\alpha - \lambda = 0$ in Equation 2.28, the temperature change still produces a change in the resistance because the metal wire and specimen expand by different amounts and this creates a strain and hence a change in the resistance. Suppose that λ_{gauge} and $\lambda_{specimen}$ are the linear expansion coefficients of the gauge wire and the specimen, then the differential expansion will be $\lambda_{specimen} - \lambda_{gauge}$ and this can only be zero if $\lambda_{gauge} = \lambda_{specimen}$.

2.4 RESISTIVITY OF MIXTURES AND POROUS MATERIALS

2.4.1 HETEROGENEOUS MIXTURES

Nordheim's rule only applies to solid solutions that are single-phase solids. In other words, it is valid for homogeneous mixtures in which the atoms are mixed at the atomic level throughout the solid, as in the Cu–Ni alloy. The classic problem of determining the effective resistivity of a multiphase solid is closely related to the evaluation of the effective dielectric constant, effective thermal conductivity, effective elastic modulus, effective Poisson's ratio, etc., for a variety of mixtures, including such composite materials as fiberglass. Indeed, many of the mixture rules are identical.

Consider a material with two distinct phases α and β, which are stacked in layers as illustrated in Figure 2.13a. Let us evaluate the effective resistivity for current flow in the x direction. Since the layers are in series, the effective resistance R_{eff} for the whole material is

Effective resistance

$$R_{eff} = \frac{L_\alpha \rho_\alpha}{A} + \frac{L_\beta \rho_\beta}{A} \qquad [2.29]$$

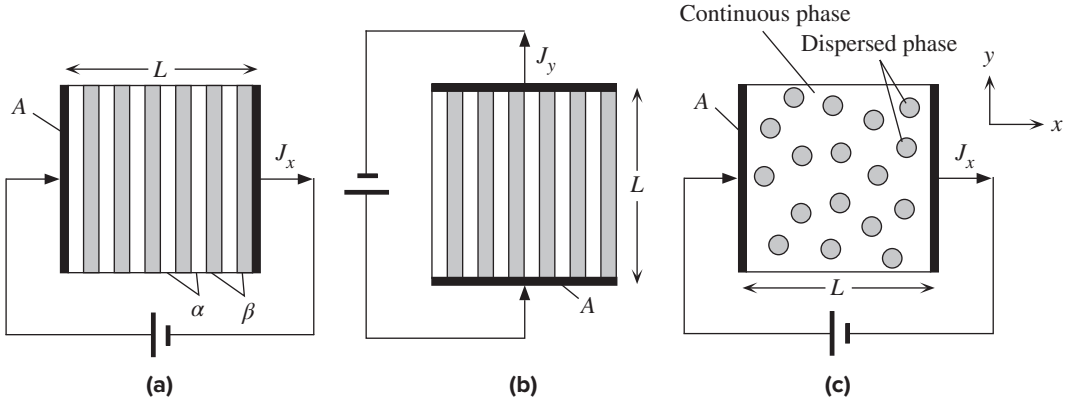


Figure 2.13 The effective resistivity of a material with a layered structure. (a) Along a direction perpendicular to the layers. (b) Along a direction parallel to the plane of the layers. (c) Materials with a dispersed phase in a continuous matrix.

where L_α is the total length (thickness) of the α-phase layers, and L_β is the total length of the β-phase layers, $L_\alpha + L_\beta = L$ is the length of the sample, and A is the cross-sectional area. Let χ_α and χ_β be the volume fractions of the α and β phases. The effective resistance is defined by

$$R_{\text{eff}} = \frac{L\rho_{\text{eff}}}{A}$$

where ρ_{eff} is the **effective resistivity.** Using $\chi_\alpha = L_\alpha/L$ and $\chi_\beta = L_\beta/L$ in Equation 2.29, we find

Resistivity–mixture rule

$$\rho_{\text{eff}} = \chi_\alpha\rho_\alpha + \chi_\beta\rho_\beta \qquad [2.30]$$

which is called the **resistivity–mixture rule** (or the **series rule of mixtures**).

If we are interested in the effective resistivity in the y direction, as shown in Figure 2.13b, obviously the α and β layers are in parallel, so an effective conductivity could be calculated in the same way as we did for the series case to find the **parallel rule of mixtures,** that is,

Conductivity–mixture rule

$$\sigma_{\text{eff}} = \chi_\alpha\sigma_\alpha + \chi_\beta\sigma_\beta \qquad [2.31]$$

where σ is the electrical conductivity of those phases identified by the subscript. Notice that the parallel rule uses the conductivity, and the series rule uses the resistivity. Equation 2.31 is often referred to as the **conductivity–mixture rule.**

Although these two rules refer to special cases, in general, for a random mixture of phase α and phase β, we would not expect either equation to apply rigorously. When the resistivities of two randomly mixed phases are not markedly different, the series mixture rule can be applied at least approximately, as we will show in Example 2.14.

However, if the resistivity of one phase is appreciably different than the other, there are two semiempirical rules that are quite useful in materials engineering.[9] Consider a heterogeneous material that has a dispersed phase (labeled d), in the form of particles, in a continuous phase (labeled c) that acts as a matrix, as depicted in Figure 2.13c. Assume that ρ_c and ρ_d are the resistivities of the continuous and dispersed phases, and χ_c and χ_d are their volume fractions. If the dispersed phase is much more resistive with respect to the matrix, that is, $\rho_d > 10\rho_c$, then

Mixture rule

$$\rho_{\text{eff}} = \rho_c\frac{(1 + \frac{1}{2}\chi_d)}{(1 - \chi_d)} \qquad (\rho_d > 10\rho_c) \qquad [2.32]$$

On the other hand, if $\rho_d < (\rho_c/10)$, then

Mixture rule

$$\rho_{\text{eff}} = \rho_c\frac{(1 - \chi_d)}{(1 + 2\chi_d)} \qquad (\rho_d < 0.1\rho_c) \qquad [2.33]$$

[9] Over the years, the task of predicting the resistivity of a mixture has challenged many theorists and experimentalists, including Lord Rayleigh who, in 1892, published an excellent exposition on the subject in the Philosophical Magazine. An extensive treatment of mixtures can be found in a paper by J. A. Reynolds and J. M. Hough published in 1957 (Proceedings of the Physical Society (London), 70, 769), which contains most of the mixture rules that are widely used today.

We therefore have at least four mixture rules at our disposal, the uses of which depend on the mixture geometry and the resistivities of the various phases. The problem is identifying which one to use for a given material, which in turn requires a knowledge of the microstructure and properties of the constituents. It should be emphasized that, at best, Equations 2.30 to 2.33 provide only a reasonable estimate of the effective resistivity of the mixture.[10]

Equations 2.32 and 2.33 are simplified special cases of a more general mixture rule due to **Reynolds and Hough** (1957). Consider a mixture that consists of a continuous conducting phase with a conductivity σ_c that has dispersed spheres of another phase of conductivity σ_d and of volume fraction χ, similar to Figure 2.13c. The effective conductivity σ_{eff} of the mixture is given by

Reynolds and Hough rule for mixture of dispersed phases

$$\frac{\sigma_{\text{eff}} - \sigma_c}{\sigma_{\text{eff}} + 2\sigma_c} = \chi \frac{\sigma_d - \sigma_c}{\sigma_d + 2\sigma_c} \qquad [2.34]$$

It is assumed that the spheres are randomly dispersed in the material. It is left as an exercise to show that if $\sigma_d \ll \sigma_c$, then Equation 2.34 reduces to Equation 2.32. A good application would be the calculation of the effective resistivity of porous carbon electrodes, which can be 50–100 percent more resistive than bulk polycrystalline carbon (graphite). If, on the other hand, $\sigma_d \gg \sigma_c$, the dispersed phase is very conducting, for example, silver particles mixed into a graphite paste to increase the conductivity of the paste, then Equation 2.34 reduces to Equation 2.33. The usefulness of Equation 2.34 cannot be underestimated inasmuch as there are many types of materials in engineering that are mixtures of one type or another.

EXAMPLE 2.14 **THE RESISTIVITY-MIXTURE RULE** Consider a two-phase alloy consisting of phase α and phase β randomly mixed as shown in Figure 2.14a. The solid consists of a random mixture of two types of resistivities, ρ_α of α and ρ_β of β. We can divide the solid into a bundle of N parallel fibers of length L and cross-sectional area A/N, as shown in Figure 2.14b. In this fiber (infinitesimally thin), the α and β phases are in series, so if $\chi_\alpha = V_\alpha/V$ is the volume fraction of phase α and χ_β is that of β, then the total length of all α regions present in the fiber is $\chi_\alpha L$, and the total length of β regions is $\chi_\beta L$. The two resistances are in series, so the fiber resistance is

$$R_{\text{fiber}} = \frac{\rho_\alpha(\chi_\alpha L)}{(A/N)} + \frac{\rho_\beta(\chi_\beta L)}{(A/N)}$$

But the resistance of the solid is made up of N such fibers in parallel, that is,

$$R_{\text{solid}} = \frac{R_{\text{fiber}}}{N} = \frac{\rho_\alpha \chi_\alpha L}{A} + \frac{\rho_\beta \chi_\beta L}{A}$$

By definition, $R_{\text{solid}} = \rho_{\text{eff}} L/A$, where ρ_{eff} is the effective resistivity of the material, so

$$\frac{\rho_{\text{eff}} L}{A} = \frac{\rho_\alpha \chi_\alpha L}{A} + \frac{\rho_\beta \chi_\beta L}{A}$$

[10] More accurate mixture rules have been established for various types of mixtures with components possessing widely different properties, which the keen reader can find in P. L. Rossiter, *The Electrical Resistivity of Metals and Alloys,* Cambridge University Press, Cambridge, 1987.

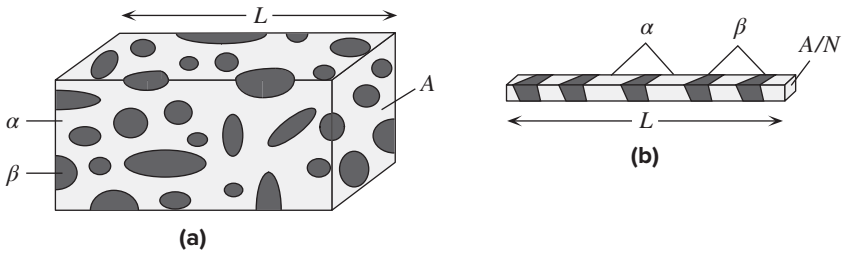


Figure 2.14 (a) A two-phase solid. (b) A thin fiber cut out from the solid.

Thus, for a two-phase solid, the effective resistivity will be

Resistivity mixture rule

$$\rho_{\text{eff}} = \chi_\alpha \rho_\alpha + \chi_\beta \rho_\beta$$

If the densities of the two phases are not too different, we can use weight fractions instead of volume fractions. The series rule fails when the resistivities of the phases are vastly different. A major (and critical) tacit assumption here is that the current flow lines are all parallel, so that no current crosses from one fiber to another. Only then can we say that the effective resistance is R_{fiber}/N. Further, notice that the rule fails when one phase has infinite resistivity even if its volume fraction is very small.

EXAMPLE 2.15

A COMPONENT WITH DISPERSED AIR PORES What is the effective resistivity of 95/5 (95% Cu–5% Sn) bronze, which is made from powdered metal containing dispersed pores at 15% (volume percent, vol.%). The resistivity of 95/5 bronze is $1 \times 10^{-7}\ \Omega$ m.

SOLUTION

Pores are infinitely more resistive ($\rho_d = \infty$) than the bronze matrix, so we use Equation 2.32,

$$\rho_{\text{eff}} = \rho_c \frac{1 + \frac{1}{2}\chi_d}{1 - \chi_d} = (1 \times 10^{-7}\ \Omega\ \text{m}) \frac{1 + \frac{1}{2}(0.15)}{1 - 0.15} = 1.27 \times 10^{-7}\ \Omega\ \text{m}$$

EXAMPLE 2.16

COMBINED NORDHEIM AND MIXTURE RULES Brass is an alloy composed of Cu and Zn. The alloy is a solid solution for Zn content less than 30 wt.%. Consider a brass component made from sintering 90 at.% Cu and 10 at.% Zn brass powder. The component contains dispersed air pores at 15% (vol.%). The Nordheim coefficient C of Zn in Cu is 300 nΩ m, under very dilute conditions. Each Zn atom donates two, whereas each Cu atom of the matrix donates one conduction electron, so that the Cu–Zn alloy has a higher electron concentration than in the Cu crystal itself. Predict the effective resistivity of this brass component.

SOLUTION

We first calculate the resistivity of the alloy without the pores, which forms the continuous phase in the powdered material. The simple Nordheim's rule predicts that

$$\rho_{\text{brass}} = \rho_{\text{copper}} + CX(1 - X) = 17\ \text{n}\Omega\ \text{m} + 300(0.1)(1 - 0.1) = 44\ \text{n}\Omega\ \text{m}$$

The experimental value, about 40 nΩ m, is actually less because Zn has a valency of 2, and when a Zn atom replaces a host Cu atom, it donates two electrons instead of one. We can very roughly adjust the calculated resistivity by noting that a 10 at.% Zn addition increases the conduction electron concentration by 10% and hence reduces the resistivity ρ_{brass} by 10% to 40 nΩ m.

The powdered metal has $\chi_d = 0.15$, which is the volume fraction of the dispersed phase, that is, the air pores, and $\rho_c = \rho_{\text{brass}} = 40$ nΩ m is the resistivity of the continuous matrix. The effective resistivity of the powdered metal is given by

$$\rho_{\text{eff}} = \rho_c \frac{1 + \frac{1}{2}\chi_d}{1 - \chi_d} = (40 \text{ n}\Omega \text{ m}) \frac{1 + \frac{1}{2}(0.15)}{1 - (0.15)} = 50.6 \text{ n}\Omega \text{ m}$$

If we use the simple conductivity mixture rule, ρ_{eff} is 47.1 nΩ m, and it is underestimated.

The *effective* Nordheim coefficient C_{eff} at the composition of interest is about 255 nΩ m, which would give $\rho_{\text{brass}} = \rho_o + C_{\text{eff}}X(1 - X) = 40$ nΩ m. It is left as an exercise to show that the effective number of conduction electrons per atom in the alloy is $1 + X$ so that we must divide the ρ_{brass} calculated above by $(1 + X)$ to obtain the correct resistivity of brass if we use the listed value of C under dilute conditions. (See Question 2.10.)

2.4.2 TWO-PHASE ALLOY (Ag–Ni) RESISTIVITY AND ELECTRICAL CONTACTS

Certain binary alloys, such as Pb–Sn and Cu–Ag, only exhibit a single-phase alloy structure over very small composition ranges. For most compositions, these alloys form a two-phase heterogeneous mixture of phases α and β. A typical phase diagram for such a eutectic binary alloy system is shown in Figure 2.15a, which could be a schematic scheme for the Cu–Ag system or the Pb–Sn system. The phase diagram identifies the phases existing in the alloy at a given temperature and composition. If the overall composition X is less than X_1, then at T_1, the alloy will consist of phase α only. This phase is Cu rich. When the composition X is between X_1 and X_2, then the alloy will consist of the two phases α and β randomly mixed. The phase α is Cu

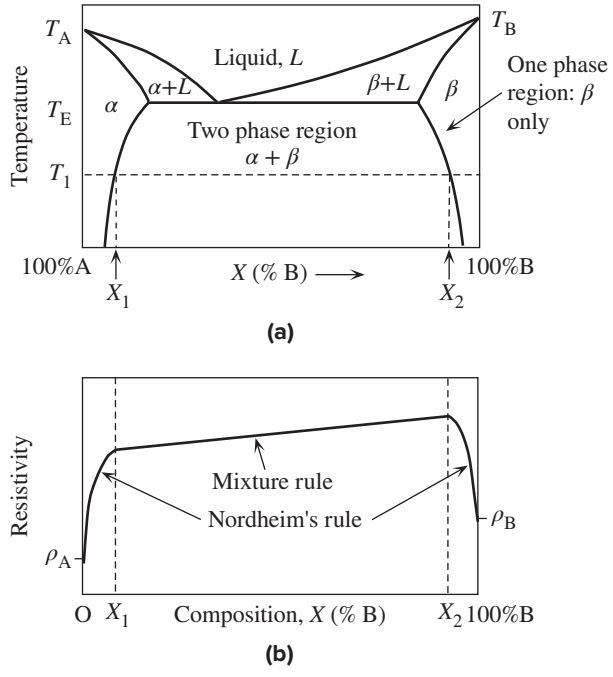


Figure 2.15 Eutectic-forming alloys, *e.g.,* Cu–Ag. (a) The phase diagram for a binary, eutectic-forming alloy. (b) The resistivity versus composition for the binary alloy.

rich (that is, it has composition X_1) and the phase β is Ag rich (composition X_2). The relative amounts of each phase are determined by the well-known **lever rule,** which means that we can determine the volume fractions of α and β, χ_α and χ_β, as the alloy composition is changed from X_1 to X_2.

For this alloy system, the dependence of the resistivity on the alloy composition is shown in Figure 2.15b. Between O and X_1 (% Ag), the solid is one phase (isomorphous); therefore, in this region, ρ increases with the concentration of Ag by virtue of Nordheim's rule. At X_1, the solubility limit of Ag in Cu is reached, and after X_1, a second phase, which is β rich, is formed. Thus, in the composition range X_1 to X_2, we have a mixture of α and β phases, so ρ is given by Equation 2.30 for mixtures and is therefore less than that for a single-phase alloy of the same composition. Similarly, at the Ag end ($X_2 < X < 100\%$), as Cu is added to Ag, between 100% Ag and the solubility limit at X_2, the resistivity is determined by Nordheim's rule. The expected behavior of the resistivity of an eutectic binary alloy over the whole composition range is therefore as depicted in Figure 2.15b.

Electrical, thermal, and other physical properties make copper the most widely used metallic conductor. For many electrical applications, high-conductivity copper, having extremely low oxygen and other impurity contents, is produced. Although aluminum has a conductivity of only 60% of that of copper, it is also frequently used as an electrical conductor. On the other hand, silver has a higher conductivity than copper, but its cost prevents its use, except in specialized applications. Switches often have silver contact specifications, though it is likely that the contact metal is actually a silver alloy. In fact, silver has the highest electrical and thermal conductivity and is consequently the natural choice for use in electrical contacts. In the form of alloys with various other metals, it is used extensively in make-and-break switching applications for currents of up to about 600 A. The precious metals, gold, platinum, and palladium, are extremely resistant to corrosion; consequently, in the form of various alloys, particularly with Ag, they are widely used in electrical contacts. For example, Ag–Ni alloys are common electrical contact materials for the switches in many household appliances.

It is frequently necessary to improve the mechanical properties of a metal alloy without significantly impairing its electrical conductivity. Solid-solution alloying improves mechanical strength, but at the expense of conductivity. A compromise must often be found between electrical and mechanical properties. Most often, strength is enhanced by introducing a second phase that does not have such an adverse effect on the conductivity. For example, Ag–Pd alloys form a solid solution such that the resistivity increases appreciably due to Nordheim's rule. The resistivity of Ag–Pd is mainly controlled by the scattering of electrons from Pd atoms randomly mixed in the Ag matrix. In contrast, Ag and Ni form a two-phase alloy, a mixture of Ag-rich and Ni-rich phases. The Ag–Ni alloy is almost as strong as the Ag–Pd alloy, but it has a lower resistivity because the mixture rule volume averages the two resistivities.

2.5 THE HALL EFFECT AND HALL DEVICES

An important phenomenon that we can comfortably explain using the "electron as a particle" concept is the Hall effect, which is illustrated in Figure 2.16. When we apply a magnetic field in a perpendicular direction to the applied field (which is driving the current), we find there is a transverse field in the sample that is perpendicular

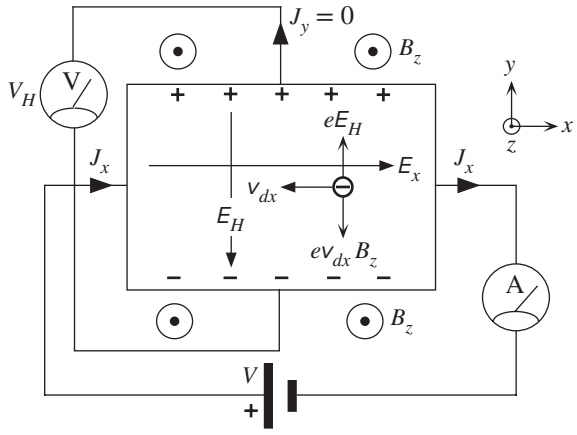


Figure 2.16 Illustration of the Hall effect. The z direction is out of the plane of the paper. The externally applied magnetic field is along the z direction.

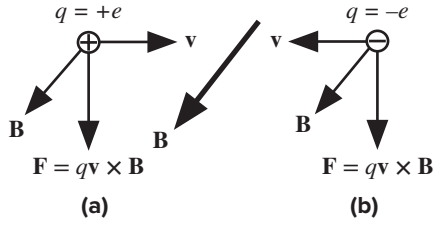


Figure 2.17 A moving charge experiences a Lorentz force in a magnetic field. (a) A positive charge moving in the x direction experiences a force downward. (b) A negative charge moving in the $-x$ direction also experiences a force downward.

to the direction of both the applied field E_x and the magnetic field B_z, that is, in the y direction. Putting a voltmeter across the sample, as in Figure 2.16, gives a voltage reading V_H. The applied field E_x drives a current J_x in the sample. The electrons move in the $-x$ direction, with a drift velocity v_{dx}. Because of the magnetic field, there is a force (called the **Lorentz force**) acting on each electron and given by $F_y = -ev_{dx}B_z$. The direction of this Lorentz force is the $-y$ direction, which we can show by applying the corkscrew rule, because, in vector notation, the force **F** acting on a charge q moving with a velocity **v** in a magnetic field **B** is given through the vector product

Lorentz force

$$\mathbf{F} = q\mathbf{v} \times \mathbf{B} \qquad [2.35]$$

All moving charges experience the Lorentz force in Equation 2.35 as shown schematically in Figure 2.17. In our example of a metal in Figure 2.16, this Lorentz force is the $-y$ direction, so it pushes the electrons downward, as a result of which there is a negative charge accumulation near the bottom of the sample and a positive charge near the top of the sample, due to exposed metal ions (*e.g.*, Cu^+).

The accumulation of electrons near the bottom results in an internal electric field E_H in the $-y$ direction. This is called the **Hall field** and gives rise to a Hall voltage V_H between the top and bottom of the sample. Electron accumulation continues until the increase in E_H is sufficient to stop the further accumulation of electrons. When this happens, the magnetic-field force $ev_{dx}B_z$ that pushes the electrons down just balances the force eE_H that prevents further accumulation. Therefore, in the steady state,

$$eE_H = ev_{dx}B_z$$

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) $\times 10^{-11}$	R_H ($m^3\ A^{-1}\ s^{-1}$) (Theory) $\times 10^{-11}$	$\mu_H = \lvert\sigma R_H\rvert$ ($cm^2\ V^{-1}\ s^{-1}$)
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.

However, $J_x = env_{dx}$. Therefore, we can substitute for v_{dx} to obtain $eE_H = J_xB_z/n$ or

$$E_H = \left(\frac{1}{en}\right)J_xB_z \qquad [2.36]$$

A useful parameter called the **Hall coefficient** R_H is defined as

Definition of Hall coefficient

$$R_H = \frac{E_y}{J_xB_z} \qquad [2.37]$$

The quantity R_H measures the resulting Hall field, along y, per unit transverse applied current and magnetic field. The larger R_H, the greater E_y for a given J_x and B_z. Therefore, R_H is a gauge of the magnitude of the Hall effect. A comparison of Equations 2.36 and 2.37 shows that for metals,

Hall coefficient for electron conduction

$$R_H = -\frac{1}{en} \qquad [2.38]$$

The reason for the negative sign is that $E_H = -E_y$, which means that E_H is in the $-y$ direction.

Inasmuch as R_H depends inversely on the free electron concentration, its value in metals is much less than that in semiconductors. In fact, Hall-effect devices (such as magnetometers) always employ a semiconductor material, simply because the R_H is larger. Table 2.4 lists the Hall coefficients of a few metals. R_H is typically negative for most metals, although there also many metals that exhibit a positive Hall coefficient (see Be in Table 2.4). The reasons for the latter involve the band theory of solids, which we will discuss in Chapter 4. Table 2.4 also shows the theoretical values for R_H calculated from Equation 2.38 by using the atomic concentration and number of expected conduction electrons. The agreement is surprisingly good for some of the metals (Al, K, Na) even though we used simple classical ideas in the derivation of R_H.[11]

[11] See Question 2.14 in which the number of conduction electrons are calculated from experimental R_H values and compared with the valency of the metal.

Since the Hall voltage depends on the product of two quantities, the current density J_x and the transverse applied magnetic field B_z, we see that the effect naturally multiplies two independently variable quantities. Therefore, it provides a means of carrying out a multiplication process. One obvious application is measuring the power dissipated in a load, where the load current and voltage are multiplied. There are many instances when it is necessary to measure magnetic fields, and the Hall effect is ideally suited to such applications. Commercial Hall-effect magnetometers can measure magnetic fields as low as 10 nT, which should be compared to the earth's magnetic field of ~50 μT. Depending on the application, manufacturers use different semiconductors to obtain the desired sensitivity. Hall-effect semiconductor devices are generally inexpensive, small, and reliable. Typical commercial, linear Hall-effect sensor devices are capable of providing a Hall voltage of ~10 mV per mT of applied magnetic field.

The Hall effect is also widely used in magnetically actuated electronic switches. The application of a magnetic field, say from a magnet, results in a Hall voltage that is amplified to trigger an electronic switch. The switches invariably use Si and are readily available from various companies. Hall-effect electronic switches are used as noncontacting keyboard and panel switches that last almost forever, as they have no mechanical contact assembly. Another advantage is that the electrical contact is "bounce" free. There are a variety of interesting applications for Hall-effect switches, ranging from ignition systems, to speed controls, position detectors, alignment controls, brushless dc motor commutators, etc.

EXAMPLE 2.17 **HALL-EFFECT WATTMETER** The Hall effect can be used to implement a wattmeter to measure electrical power dissipated in a load. The schematic sketch of the Hall-effect wattmeter is shown in Figure 2.18, where the Hall-effect sample is typically a semiconductor material (usually Si). The load current I_L passes through two coils, which are called current coils and are shown as C in Figure 2.18. These coils set up a magnetic field B_z such that $B_z \propto I_L$. The Hall-effect sample is positioned in this field between the coils. The voltage V_L across the load drives a current $I_x = V_L/R$ through the sample, where R is a series resistance that is much larger than the resistance of the sample and that of the load. Normally, the current I_x is very

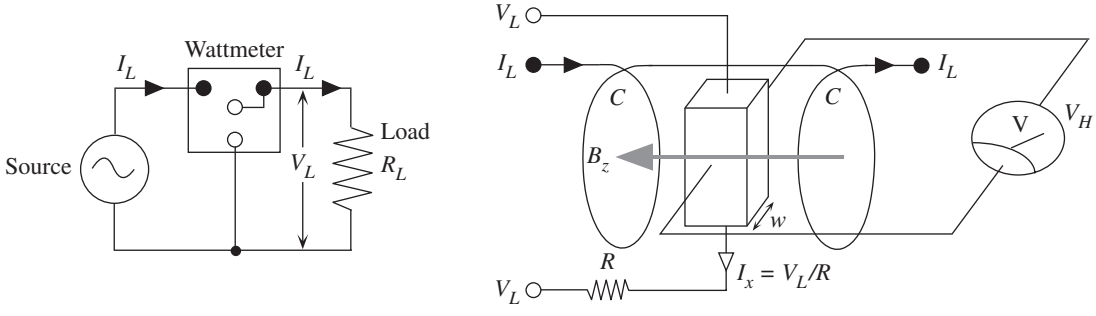


Figure 2.18 Wattmeter based on the Hall effect.

Load voltage and load current have *L* as subscript; *C* denotes the current coils for setting up a magnetic field through the Hall-effect sample (semiconductor).

small and negligible compared to the load current. If w is the width of the sample, then the measured Hall voltage is

$$V_H = wE_H = wR_H J_x B_z \propto I_x B_z \propto V_L I_L$$

which is the electrical power dissipated in the load. The voltmeter that measures V_H can now be calibrated to read directly the power dissipated in the load.

EXAMPLE 2.18

HALL MOBILITY Show that if R_H is the Hall coefficient and σ is the conductivity of a metal, then the drift mobility of the conduction electrons is given by

$$\mu_d = |\sigma R_H| \qquad [2.39]$$

The Hall coefficient and conductivity of copper at 300 K have been measured to be -0.54×10^{-10} m^3 A^{-1} s^{-1} and 5.9×10^7 Ω^{-1} m^{-1}, respectively. Calculate the drift mobility of electrons in copper.

SOLUTION

Consider the expression for

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

Since the conductivity is given by $\sigma = en\mu_d$, we can substitute for en to obtain

$$R_H = \frac{-\mu_d}{\sigma} \qquad \text{or} \qquad \mu_d = -R_H\sigma$$

which is Equation 2.39. The drift mobility can thus be determined from R_H and σ.

The product of σ and R_H is called the **Hall mobility** μ_H. Some values for the Hall mobility of electrons in various metals are listed in Table 2.4. From the expression in Equation 2.39, we get

$$\mu_d = |(-0.54 \times 10^{-10} \text{ m}^3 \text{ A}^{-1} \text{ s}^{-1})(5.9 \times 10^7 \ \Omega^{-1} \text{ m}^{-1})| = 3.2 \times 10^{-3} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$$

It should be mentioned that Equation 2.39 is an oversimplification. The actual relationship involves a numerical factor that multiplies the right term in Equation 2.39. The factor depends on the charge carrier scattering mechanism that controls the drift mobility.

EXAMPLE 2.19

CONDUCTION ELECTRON CONCENTRATION FROM THE HALL EFFECT Using the electron drift mobility from Hall-effect measurements (Table 2.4), calculate the concentration of conduction electrons in copper, and then determine the average number of electrons contributed to the free electron gas per copper atom in the solid.

SOLUTION

The number of conduction electrons is given by $n = \sigma/e\mu_d$. The conductivity of copper is 5.9×10^7 Ω^{-1} m^{-1}, whereas from Table 2.4, the electron drift mobility is 3.2×10^{-3} m^2 V^{-1} s^{-1}. So,

$$n = \frac{(5.9 \times 10^7 \ \Omega^{-1} \text{ m}^{-1})}{[(1.6 \times 10^{-19} \text{ C})(3.2 \times 10^{-3} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1})]} = 1.15 \times 10^{29} \text{ m}^{-3}$$

Since the concentration of copper atoms is 8.5×10^{28} m^{-3}, the average number of electrons contributed per atom is $(1.15 \times 10^{29} \text{ m}^{-3})/(8.5 \times 10^{28} \text{ m}^{-3}) \approx 1.36$.

2.6 THERMAL CONDUCTION

2.6.1 THERMAL CONDUCTIVITY

Experience tells us that metals are both good electrical and good thermal conductors. We may therefore surmise that the free conduction electrons in a metal must also play a role in heat conduction. Our conjecture is correct for metals, but not for other materials. The transport of heat in a metal is accomplished by the electron gas (conduction electrons), whereas in nonmetals, the conduction is due to lattice vibrations.

When a metal piece is heated at one end, the amplitude of the atomic vibrations, and thus the average kinetic energy of the electrons, in this region increases, as depicted in Figure 2.19. Electrons gain energy from energetic atomic vibrations when the two collide. By virtue of their increased random motion, these energetic electrons then transfer the extra energy to the colder regions by colliding with the atomic vibrations there. Thus, electrons act as "energy carriers."

The thermal conductivity of a material, as its name implies, measures the ease with which heat, that is, thermal energy, can be transported through the medium. Consider the metal rod shown in Figure 2.20, which is heated at one end. Heat will flow from the hot end to the cold end. Experiments show that the rate of heat flow, $Q' = dQ/dt$, through a thin section of thickness δx is proportional to the temperature gradient $\delta T/\delta x$ and the cross-sectional area A, so

Fourier's law of thermal conduction

$$Q' = -A\kappa\frac{\delta T}{\delta x} \qquad [2.40]$$

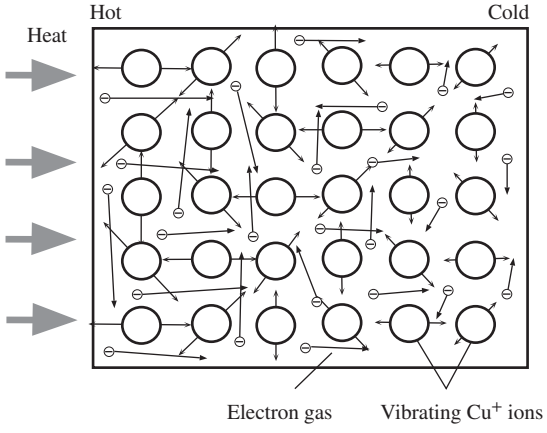


Figure 2.19 Thermal conduction in a metal involves transferring energy from the hot region to the cold region by conduction electrons.

More energetic electrons (shown with longer velocity vectors) from the hotter regions arrive at cooler regions, collide with lattice vibrations, and transfer their energy. Lengths of arrowed lines on atoms represent the magnitudes of atomic vibrations.

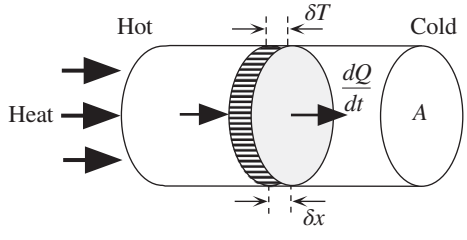


Figure 2.20 Heat flow in a metal rod heated at one end.

Consider the rate of heat flow, dQ/dt, across a thin section δx of the rod. The rate of heat flow is proportional to the temperature gradient $\delta T/\delta x$ and the cross-sectional area A.

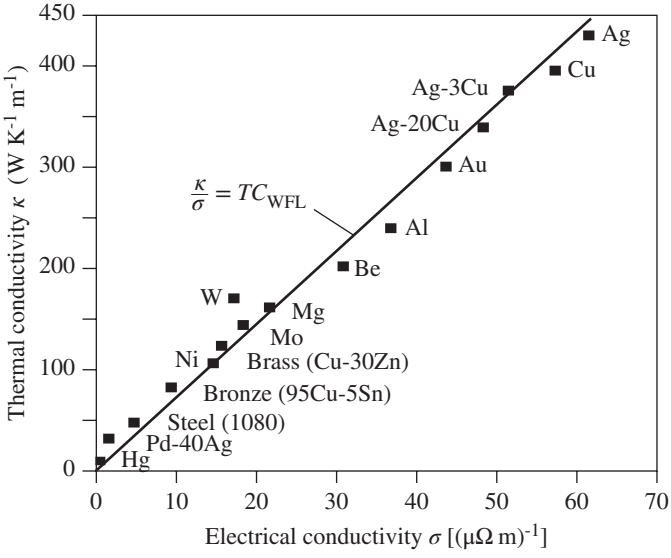


Figure 2.21 Thermal conductivity κ versus electrical conductivity σ for various metals (elements and alloys) at 20 °C.
The solid line represents the WFL law with $C_{WFL} \approx 2.44 \times 10^8$ W Ω K^{-2}.

where κ is a material-dependent **constant of proportionality** that we call the **thermal conductivity.** The negative sign indicates that the heat flow direction is that of decreasing temperature. Equation 2.40 is often referred to as **Fourier's law** of heat conduction and is a defining equation for κ. The driving force for the heat flow is the temperature gradient $\delta T/\delta x$. If we compare Equation 2.40 with Ohm's law for the electric current I, we see that

Ohm's law of electrical conduction

$$I = -A\sigma\frac{\delta V}{\delta x} \qquad [2.41]$$

which shows that in this case, the driving force is the potential gradient, that is, the electric field.[12] In metals, electrons participate in the processes of charge and heat transport, which are characterized by σ and κ, respectively. Therefore, it is not surprising to find that the two coefficients are related by the **Wiedemann–Franz–Lorenz law,**[13] which is

Wiedemann–Franz–Lorenz law

$$\frac{\kappa}{\sigma T} = C_{WFL} \qquad [2.42]$$

where $C_{WFL} = \pi^2 k^2/3e^2 = 2.44 \times 10^{-8}$ W Ω K^{-2} is a constant called the **Lorenz number** (or the Wiedemann–Franz–Lorenz coefficient).

Experiments on a wide variety of metals, ranging from pure metals to various alloys, show that Equation 2.42 is reasonably well obeyed at close to room temperature and above, as illustrated in Figure 2.21. Since the electrical conductivity of

[12] Recall that $J = \sigma E$ which is equivalent to Equation 2.41.

[13] Historically, Wiedemann and Franz noted in 1853 that κ/σ is the same for all metals at the same temperature. Lorenz in 1881 showed that κ/σ is proportional to the temperature with a proportionality constant that is nearly the same for many metals. The law stated in equation 2.42 reflects both observations. By the way, Lorenz, who was a Dane, should not be confused with Lorentz, who was Dutch.

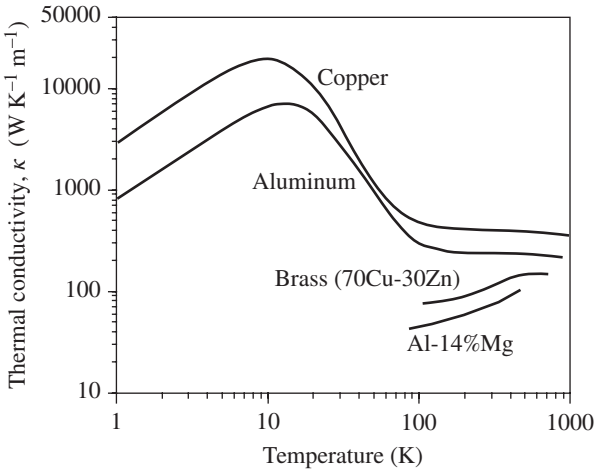


Figure 2.22 Thermal conductivity versus temperature for two pure metals (Cu and Al) and two alloys (brass and Al–14% Mg).

SOURCE: Data extracted from Touloukian, Y.S., et al., "Thermal Conductivity, Metallic Elements and Alloys," *Thermophysical Properties of Matter,* vol.1, 1970. New York, NY: Plenum, 1970.

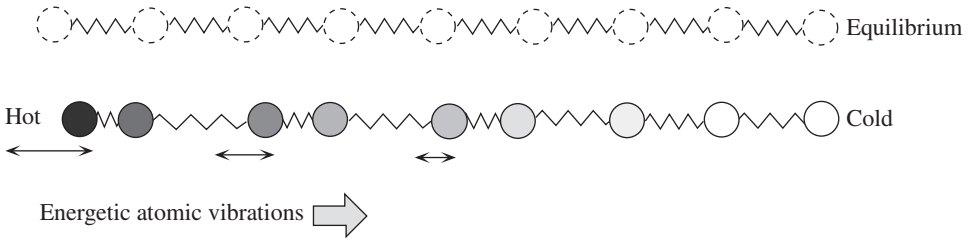


Figure 2.23 Conduction of heat in insulators involves the generation and propagation of atomic vibrations through the bonds that couple the atoms (an intuitive figure).

pure metals is inversely proportional to the temperature, we can immediately conclude that the thermal conductivity of these metals must be relatively temperature independent at room temperature and above.

Figure 2.22 shows the temperature dependence of κ for copper and aluminum down to the lowest temperatures. It can be seen that for these two metals, above $\sim$100 K, the thermal conductivity becomes temperature independent, in agreement with Equation 2.42. Qualitatively, above $\sim$100 K, κ is constant, because heat conduction depends essentially on the rate at which the electron transfers energy from one atomic vibration to another as it collides with them (Figure 2.19). This rate of energy transfer depends on the mean speed of the electron u, which increases only fractionally with the temperature. In fact, the fractionally small increase in u is more than sufficient to carry the energy from one collision to another and thereby excite more energetic lattice vibrations in the colder regions.

Nonmetals do not have any free conduction electrons inside the crystal to transfer thermal energy from hot to cold regions of the material. In nonmetals, the energy transfer involves lattice vibrations, that is, atomic vibrations of the crystal. We know that we can view the atoms and bonds in a crystal as balls connected together through springs as shown for one chain of atoms in Figure 2.23. As we know from the kinetic

Table 2.5 Typical thermal conductivities of various classes of materials at 25 °C

Material	κ (W m^{-1} K^{-1})	Material	κ (W m^{-1} K^{-1})
Pure metal		Ceramics and glasses	
Nb	52	Glass-borosilicate	0.75
Fe	80	Silica-fused (SiO_2)	1.5
Zn	113	S_3N_4	20
W	178	Alumina (Al_2O_3)	30
Al	250	Sapphire (Al_2O_3)	37
Cu	390	Beryllium (BeO)	260
Ag	420	Diamond	~1000
Metal alloys		Polymers	
Stainless steel	12–16	Polypropylene	0.12
55% Cu–45% Ni	19.5	PVC	0.17
70% Ni–30% Cu	25	Polycarbonate	0.22
1080 steel	50	Nylon 6,6	0.24
Bronze (95% Cu–5% Sn)	80	Teflon	0.25
Brass (63% Cu–37% Zn)	125	Polyethylene, low density	0.3
Dural (95% Al–4% Cu–1% Mg)	147	Polyethylene, high density	0.5

molecular theory, all the atoms would be vibrating and the average vibrational kinetic energy would be proportional to the temperature. Intuitively, as depicted in Figure 2.23, when we heat one end of a crystal, we set up large-amplitude atomic vibrations at this hot end. The springs *couple* the vibrations to neighboring atoms and thus allow the large-amplitude vibrations to propagate, as a **vibrational wave,** to the cooler regions of the crystal. If we were to grab the left-end atom in Figure 2.23 and vibrate it violently, we would be sending vibrational waves down the ball-spring-ball chain. The efficiency of heat transfer depends not only on the efficiency of coupling between the atoms, and hence on the nature of interatomic bonding, but also on how the vibrational waves propagate in the crystal and how they are scattered by crystal imperfections and by their interactions with other vibrational waves; this topic is discussed in Chapter 4. The stronger the coupling, the greater will be the thermal conductivity, a trend that is intuitive but also borne out by experiments. Diamond has an exceptionally strong covalent bond and also has a very high thermal conductivity; $\kappa \approx 1000$ W m^{-1} K^{-1}. On the other hand, polymers have weak secondary bonding between the polymer chains and their thermal conductivities are very poor; $\kappa < 1$ W m^{-1} K^{-1}.

The thermal conductivity, in general, depends on the temperature. Different classes of materials exhibit different κ values and also different κ versus T behavior. Table 2.5 summarizes κ at room temperature for various classes of materials. Notice how ceramics have a very large range of κ values.

EXAMPLE 2.20

THERMAL CONDUCTIVITY A 95/5 (95% Cu–5% Sn) bronze bearing made of powdered metal contains 15% (vol.%) porosity. Calculate its thermal conductivity at 300 K, given that the electrical conductivity of 95/5 bronze is 10^7 Ω^{-1} m^{-1}.

SOLUTION

Recall that in Example 2.15, we found the electrical resistivity of the same bronze by using the mixture rule in Equation 2.32 in Section 2.4. We can use the same mixture rule again here, but we need the thermal conductivity of 95/5 bronze. From $\kappa/\sigma T = C_{\text{WFL}}$, we have

$$\kappa = \sigma T C_{\text{WFL}} = (1 \times 10^7)(300)(2.44 \times 10^{-8}) = 73.2 \text{ W m}^{-1} \text{ K}^{-1}$$

Thus, the effective thermal conductivity is

$$\frac{1}{\kappa_{\text{eff}}} = \frac{1}{\kappa_c}\left[\frac{1 + \frac{1}{2}\chi_d}{1 - \chi_d}\right] = \frac{1}{(73.2 \text{ W m}^{-1} \text{ K}^{-1})}\left[\frac{1 + \frac{1}{2}(0.15)}{1 - 0.15}\right]$$

so that

$$\kappa_{\text{eff}} = 57.9 \text{ W m}^{-1} \text{ K}^{-1}$$

2.6.2 THERMAL RESISTANCE

Consider a component of length L that has a temperature difference ΔT between its ends as in Figure 2.24a. The temperature gradient is $\Delta T/L$. Thus, the rate of heat flow Q', or the **heat current,** is

Fourier's law

$$Q' = A\kappa\frac{\Delta T}{L} = \frac{\Delta T}{(L/\kappa A)} \quad [2.43]$$

This should be compared with Ohm's law in electric circuits,

Ohm's law

$$I = \frac{\Delta V}{R} = \frac{\Delta V}{(L/\sigma A)} \quad [2.44]$$

where ΔV is the voltage difference across a conductor of resistance R, and I is the electric current.

In analogy with electrical resistance, we may define **thermal resistance** θ by

Definition of thermal resistance

$$Q' = \frac{\Delta T}{\theta} \quad [2.45]$$

where, in terms of thermal conductivity,

Thermal resistance

$$\theta = \frac{L}{\kappa A} \quad [2.46]$$

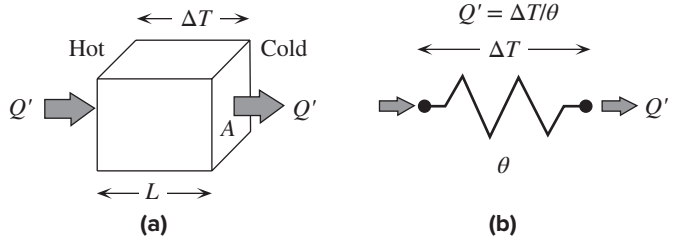


Figure 2.24 Conduction of heat through a component in (a) can be modeled as a thermal resistance θ shown in (b) where $Q' = \Delta T/\theta$.

The rate of heat flow Q' and the temperature difference ΔT correspond to the electric current I and potential difference ΔV, respectively. Thermal resistance is the thermal analog of electrical resistance and its thermal circuit representation is shown in Figure 2.24b.

EXAMPLE 2.21

THERMAL RESISTANCE A brass disk of electrical resistivity 50 nΩ m conducts heat from a heat source to a heat sink at a rate of 10 W. If its diameter is 20 mm and its thickness is 30 mm, what is the temperature drop across the disk, neglecting the heat losses from the surface?

SOLUTION

We first determine the thermal conductivity:

$$\kappa = \sigma T C_{\text{WFL}} = (5 \times 10^{-8}\ \Omega\ \text{m})^{-1}(300\ \text{K})(2.44 \times 10^{-8}\ \text{W}\ \Omega\ \text{K}^{-2})$$
$$= 146\ \text{W m}^{-1}\ \text{K}^{-1}$$

The thermal resistance is

$$\theta = \frac{L}{\kappa A} = \frac{(30 \times 10^{-3}\ \text{m})}{(146\ \text{W m}^{-1}\ \text{K}^{-1})\pi(10 \times 10^{-3}\ \text{m})^2} = 0.65\ \text{K W}^{-1}$$

Therefore, the temperature drop is

$$\Delta T = \theta Q' = (0.65\ \text{K W}^{-1})(10\ \text{W}) = 6.5\ \text{K or °C}$$

2.7 ELECTRICAL CONDUCTIVITY OF NONMETALS

All metals are good conductors because they have a very large number of conduction electrons free inside the metal. We should therefore expect solids that do not have metallic bonding to be very poor conductors, indeed insulators. Figure 2.25 shows

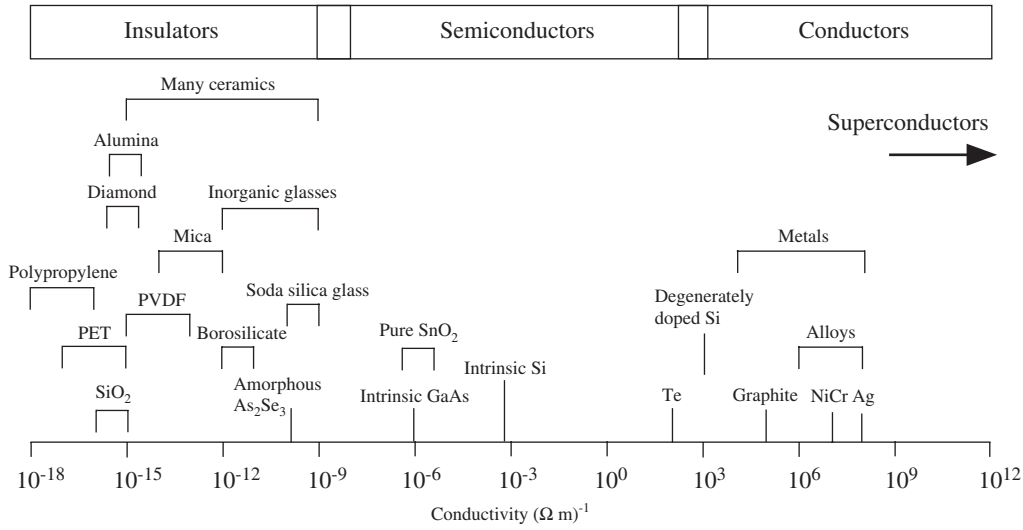


Figure 2.25 Range of conductivities exhibited by various materials.

the range of conductivities exhibited by a variety of solids. Based on typical values of the conductivity, it is possible to empirically classify various materials into conductors, semiconductors, and insulators as in Figure 2.25. It is apparent that nonmetals are not perfect insulators with zero conductivity. There is no well-defined sharp boundary between what we call insulators and semiconductors. Conductors are intimately identified with metals. It is more appropriate to view insulators as **high resistivity** (or **low conductivity**) **materials.** In general terms, current conduction is due to the drift of mobile charge carriers through a solid by the application of an electric field. Each of the drifting species of charge carriers contributes to the observed current. In metals, there are only free electrons. In nonmetals there are other types of charge carriers that can drift.

2.7.1 SEMICONDUCTORS

A perfect Si crystal has each Si atom bonded to four neighbors, and each covalent bond has two shared electrons as we had shown in Figure 1.61a. We know from classical physics (the kinetic molecular theory and Boltzmann distribution) that all the atoms in the crystal are executing vibrations with a distribution of energies. As the temperature increases, the distribution spreads to higher energies. Statistically some of the atomic vibrations will be sufficiently energetic to rupture a bond as indicated in Figure 2.26a. This releases an electron from the bond which is *free* to wander inside the crystal. The free electron can drift in the presence of an applied field; it is called a **conduction electron.** As an electron has been removed from a region of the crystal that is otherwise neutral, the broken-bond region has a *net positive charge*. This broken-bond region is called a **hole** (h^+). An electron in a neighboring bond can jump and repair this bond and thereby create a hole in its

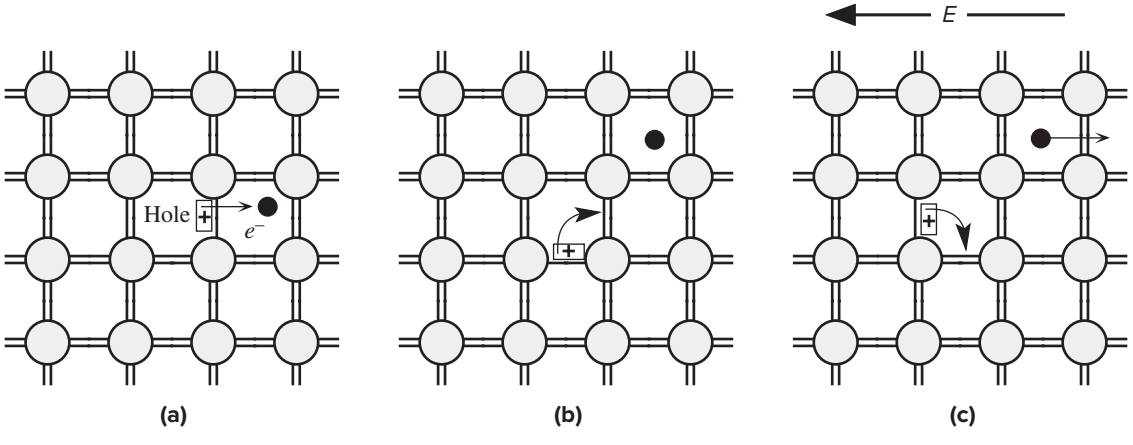


Figure 2.26 (a) Thermal vibrations of the atoms rupture a bond and release a free electron into the crystal. A hole is left in the broken bond, which has an effective positive charge. (b) An electron in a neighboring bond can jump and repair this bond and thereby create a hole in its original site; the hole has been displaced. (c) When a field is applied, both holes and electrons contribute to electrical conduction.

original site as shown in Figure 2.26b. Effectively, the hole has been displaced in the opposite direction to the electron jump by this *bond switching*. Holes can also wander in the crystal by the repetition of bond switching. When a field is applied, both holes and electrons contribute to electrical conduction as in Figure 2.26c. For all practical purposes, these holes behave as if they were *free* positively charged particles (independent of the original electrons) inside the crystal. In the presence of an applied field, holes drift along the field direction and contribute to conduction just as the free electrons released from the broken bonds drift in the opposite direction and contribute to conduction.

It is also possible to create free electrons or holes by intentionally doping a semiconductor crystal, that is substituting impurity atoms for some of the Si atoms. Defects can also generate free carriers. The simplest example is nonstoichiometric ZnO that is shown in Figure 1.57b which has excess Zn. The electrons from the excess Zn are free to wander in the crystal and hence contribute to conduction.

Suppose that n and p are the concentrations of electrons and holes in a semiconductor crystal. If electrons and holes have drift mobilities of μ_e and μ_h, respectively, then the overall conductivity of the crystal is given by

Conductivity of a semiconductor

$$\sigma = ep\mu_h + en\mu_e \qquad [2.47]$$

Unless a semiconductor has been heavily doped, the concentrations n and p are much smaller than the electron concentration in a metal. Even though carrier drift mobilities in most semiconductors are higher than electron drift mobilities in metals, semiconductors have much lower conductivities due to their lower concentration of free charge carriers.

EXAMPLE 2.22

HALL EFFECT IN SEMICONDUCTORS The hall effect in a sample where there are both negative and positive charge carriers, for example, electrons and holes in a semiconductor, involves not only the concentrations of electrons and holes, n and p, respectively, but also the electron and hole drift mobilities, μ_e and μ_h. We first have to reinterpret the relationship between the drift velocity and the electric field E.

If μ_e is the drift mobility and v_e is the drift velocity of the electrons, then we already know that $v_e = \mu_e E$. This has been derived by considering the *net electrostatic force* eE acting on a single electron and the imparted acceleration $a = eE/m_e$. The drift is therefore due to the net force $F_{\text{net}} = eE$ experienced by a conduction electron. If we were to keep eE as the *net force* F_{net} acting on a single electron, then we would have found

Drift velocity and net force

$$v_e = \frac{\mu_e}{e} F_{\text{net}} \qquad [2.48]$$

Equation 2.48 emphasizes the fact that drift is due to a net force F_{net} acting on an electron. A similar expression would also apply to the drift of a hole in a semiconductor.

When both electrons and holes are present in a semiconductor sample, both charge carriers experience a Lorentz force in the same direction since they would be drifting in the opposite directions as illustrated in Figure 2.27. Thus, both holes and electrons tend to pile near the bottom surface. The magnitude of the Lorentz force, however, will be different since the drift mobilities and hence drift velocities will be different in general. Once equilibrium is reached, there should be no current flowing in the y direction as we have an open circuit. Suppose that more holes have accumulated near the bottom surface so there is a built-in

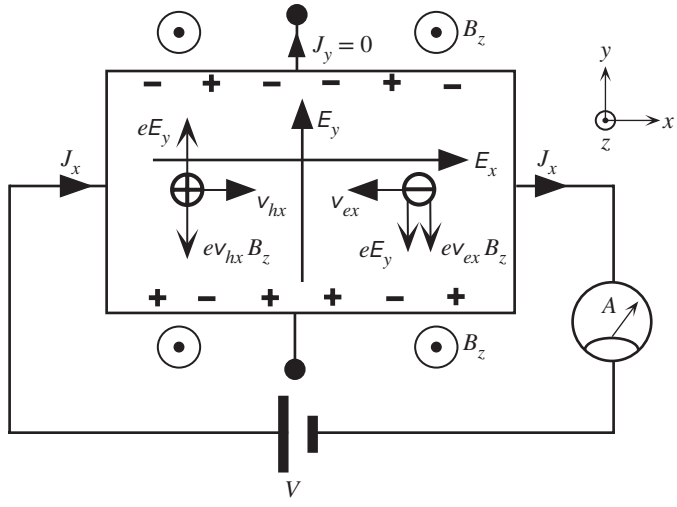


Figure 2.27 Hall effect for ambipolar conduction as in a semiconductor where there are both electrons and holes.

The magnetic field B_z is out from the plane of the paper. Both electrons and holes are deflected toward the bottom surface of the conductor and consequently the Hall voltage depends on the relative mobilities and concentrations of electrons and holes.

electric field E_y along y as shown in Figure 2.27. Suppose that v_{ey} and v_{hy} are the *usual* electron and hole drift velocities in the $-y$ and $+y$ directions, respectively, as if the electric field E_y existed alone in the $+y$ direction. The net current along y is zero, which means that

$$J_y = J_h + J_e = epv_{hy} + env_{ey} = 0 \qquad [2.49]$$

From Equation 2.49 we obtain

$$pv_{hy} = -nv_{ey} \qquad [2.50]$$

We note that either the electron or the hole drift velocity must be reversed from its usual direction; for example, holes drifting in the opposite direction to E_y. The net force acting on the charge carriers cannot be zero. This is impossible when two types of carriers are involved and both carriers are drifting along y to give a net current J_y that is zero. This is what Equation 2.49 represents. We therefore conclude that, along y, both the electron and the hole must experience a driving force to drift them. The net force experienced by the carriers, as shown in Figure 2.27, is

$$F_{hy} = eE_y - ev_{hx}B_z \qquad \text{and} \qquad -F_{ey} = eE_y + ev_{ex}B_z \qquad [2.51]$$

where v_{hx} and v_{ex} are the hole and electron drift velocities, respectively, along x. In general, the drift velocity is determined by the net force acting on a charge carrier; that is, from Equation 2.48

$$F_{hy} = \frac{ev_{hy}}{\mu_h} \qquad \text{and} \qquad -F_{ey} = \frac{ev_{ey}}{\mu_e}$$

so that Equation 2.51 becomes,

$$\frac{ev_{hy}}{\mu_h} = eE_y - ev_{hx}B_z \qquad \text{and} \qquad \frac{ev_{ey}}{\mu_e} = eE_y + ev_{ex}B_z$$

where v_{hy} and v_{ey} are the hole and electron drift velocities along y. Substituting $v_{hx} = \mu_h E_x$ and $v_{ex} = \mu_e E_x$, these become

$$\frac{v_{hy}}{\mu_h} = E_y - \mu_h E_x B_z \qquad \text{and} \qquad \frac{v_{ey}}{\mu_e} = E_y + \mu_e E_x B_z \qquad [2.52]$$

From Equation 2.52 we can substitute for v_{hy} and v_{ey} in Equation 2.50 to obtain

$$p\mu_h E_y - p\mu_h^2 E_x B_z = -n\mu_e E_y - n\mu_e^2 E_x B_z$$

or

$$E_y(p\mu_h + n\mu_e) = B_z E_x(p\mu_h^2 - n\mu_e^2) \quad [2.53]$$

We now consider what happens along the x direction. The total current density is finite and is given by the usual expression,

Current density along x

$$J_x = epv_{hx} + env_{ex} = (p\mu_h + n\mu_e)eE_x \quad [2.54]$$

We can use Equation 2.54 to substitute for E_x in Equation 2.53, to obtain

$$eE_y(n\mu_e + p\mu_h)^2 = B_z J_x(p\mu_h^2 - n\mu_e^2)$$

The Hall coefficient, by definition, is $R_H = E_y/J_x B_z$, so

Hall effect for ambipolar conduction

$$R_H = \frac{p\mu_h^2 - n\mu_e^2}{e(p\mu_h + n\mu_e)^2} \quad [2.55]$$

or

Hall effect for ambipolar conduction

$$R_H = \frac{p - nb^2}{e(p + nb)^2} \quad [2.56]$$

where $b = \mu_e/\mu_h$. It is clear that the Hall coefficient depends on both the drift mobility ratio and the concentrations of holes and electrons. For $p > nb^2$, R_H will be positive and for $p < nb^2$, it will be negative. We should note that when only one type of carrier is involved, for example, electrons only, the $J_y = 0$ requirement means that $J_y = env_{ey} = 0$, or $v_{ey} = 0$. The drift velocity along y can only be zero, if the net driving force F_{ey} along y is zero. This occurs when $eE_y - ev_{ex}B_z = 0$, that is, when the Lorentz force just balances the force due to the built-in field.

EXAMPLE 2.23

HALL COEFFICIENT OF INTRINSIC SILICON At room temperature, a pure silicon crystal (called **intrinsic silicon**) has electron and hole concentrations $n = p = n_i = 1.0 \times 10^{10}$ cm^{-3}, and electron and hole drift mobilities $\mu_e = 1350$ cm^2 V^{-1} s^{-1} and $\mu_h = 450$ cm^2 V^{-1} s^{-1}. Calculate the Hall coefficient and compare it with a typical metal.

SOLUTION

Given $n = p = n_i = 1.0 \times 10^{10}$ cm^{-3}, $\mu_e = 1350$ cm^2 V^{-1} s^{-1}, and $\mu_h = 450$ cm^2 V^{-1} s^{-1}, we have

$$b = \frac{\mu_e}{\mu_h} = \frac{1350}{450} = 3$$

Then from Equation 2.56,

$$R_H = \frac{(1.0 \times 10^{16}\,\text{m}^{-3}) - (1.0 \times 10^{16}\,\text{m}^{-3})(3)^2}{(1.6 \times 10^{-19}\,\text{C})[(1.0 \times 10^{16}\,\text{m}^{-3}) + (1.0 \times 10^{16}\,\text{m}^{-3})(3)]^2}$$
$$= -312\,\text{m}^3\,\text{A}^{-1}\,\text{s}^{-1}$$

which is orders of magnitude larger than that for a typical metal. All Hall-effect devices use a semiconductor rather than a metal sample.
