

CHAPTER 4 METALS I: THE FREE-ELECTRON MODEL

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*Freedom has a thousand charms to show,
That slaves, howe'er contented, never know.*

William Cowper

4.1 INTRODUCTION

Metals are of great importance in our daily lives. Iron is used in automobiles, copper in electrical wiring, silver and gold as jewelry, to give only a few examples. These and other metals have played an exceedingly important role in the growth of our technological, industrial world from early historical times to the present, and will continue to do so in the future.

Metals are characterized by common physical properties: great physical strength, high density, good electrical and thermal conductivities, and high optical reflectivity, which is responsible for their characteristic lustrous appearance. The explanation of these properties is important to the physicist who is interested in understanding the microscopic structure of materials, and also to the metallurgist and engineer who wish to use metals for practical purposes.

In this chapter we shall see that these properties are intimately related. They can all be explained by assuming that a metal contains a large concentration of essentially free electrons which are able to move throughout the crystal. In the introductory sections we develop the concept of the free-electron model. We then describe how electrons can carry a current in the presence of an electric field. After that we shall calculate the specific heat of electrons, and show that agreement with experiment can be obtained only if the electrons obey the Pauli exclusion principle. This introduces the important concepts of the Fermi level and Fermi surface, which are then employed to develop a more refined description of electrical and thermal conduction in metals.

The effects of a magnetic field on the motion of free electrons will also be discussed. We shall point out, in particular, how cyclotron resonance and measurements of the Hall effect can yield basic information on metals.

Some of the most interesting properties are associated with metals when studied in the optical frequency range. We shall discuss these in some detail, and show that the free-electron model is capable of explaining most of the observed properties. We shall also discuss thermionic emission of electrons from metals. Then, finally, we shall criticize the free-electron model, and discuss its limitations.

4.2 CONDUCTION ELECTRONS

What are the conduction electrons? Let us answer this question by an example, using the simplest metal, Na, as illustration. Consider first an Na gas, which is a collection of free atoms, each atom having 11 electrons orbiting around the nucleus. In chemistry these electrons are grouped into two classes: The 10 core electrons which comprise the stable structure of the filled first and second shells (Bohr orbits), and a *valence electron* loosely bound to the rest of the system. This valence electron, which occupies the third atomic shell, is the electron which is responsible for most of the ordinary chemical properties of Na. In chemical reactions the Na atom usually loses this valence electron—it being loosely bound—and an Na^+ ion is formed. This is what happens, for example, in NaCl , in which the electron is transferred from the Na to the Cl atom. The radius of the third shell in Na is 1.9 Å.

Let us now bring the Na atoms together to form a metal. In the metallic state, Na has a bcc structure (Section 1.7), and the distance between nearest neighbors is 3.7 Å. We see from Fig. 4.1 that in the solid state two atoms overlap slightly. From this observation it follows that a valence electron is no longer attached to a particular ion, but belongs to both neighboring ions at the same time. This idea can be carried a step further: A valence electron really belongs to the whole crystal, since it can move readily from one ion to its neighbor, and then the neighbor's neighbor, and so on. This mobile electron, which is called a valence electron in a free atom, becomes a *conduction electron* in a solid.

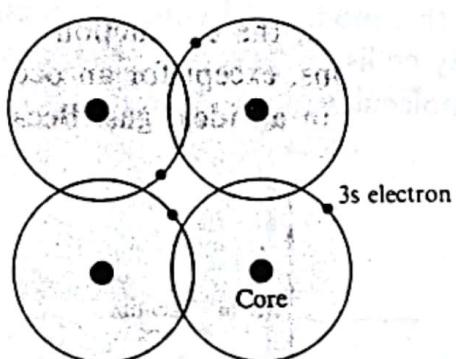


Fig 4.1 Overlap of the 3s orbitals in solid sodium.

Of course, each atom contributes its own conduction electron, and each of these electrons belongs to the whole crystal. These are called conduction electrons because they can carry an electric current under the action of an electric field. The conduction is possible because each conduction electron is spread throughout the solid (delocalized) rather than being attached to any particular atom. On the contrary, well localized electrons do not carry a current. For example, the *core electrons* in metallic Na—i.e., those centered around the nuclei at the lattice sites—do not contribute anything to the electric current. The states of these electrons in the solid differ little from those in the free atom.

In summary: When free atoms form a metal, all the valence electrons become conduction electrons and their states are profoundly modified, while the core electrons remain localized and their character remains essentially unchanged. Just as valence electrons are responsible for chemical properties, so conduction electrons are responsible for most of the properties of metals, as we shall see.

One can calculate the number of conduction electrons from the valence of the metal and its density. Thus in Na the number of conduction electrons is the same as the number of atoms, and the same is true for K, and also for the noble metals Cu, Ag, Au, all of which are monovalent. In divalent metals—such as Be, Mg, Zn, and Cd—the number of electrons is twice the number of atoms, and so on. If the density of the substance is ρ_m , then the atom concentration is

$(\rho_m/M')N_A$, where M' is the atomic weight and N_A is Avogadro's number. Denoting the atomic valence by Z_v , one finds the electron concentration[†]

$$N = Z_v \frac{\rho_m N_A}{M'}. \quad (4.1)$$

4.3 THE FREE-ELECTRON GAS

In the free-electron model, which is the basis of this chapter, the conduction electrons are assumed to be completely *free*, except for a potential at the surface (see Fig. 4.2), which has the effect of confining the electrons to the interior of the specimen. According to this model, the conduction electrons move about inside the specimen without any collisions, except for an occasional reflection from the surface, much like the molecules in an ideal gas. Because of this, we speak of a *free-electron gas*.

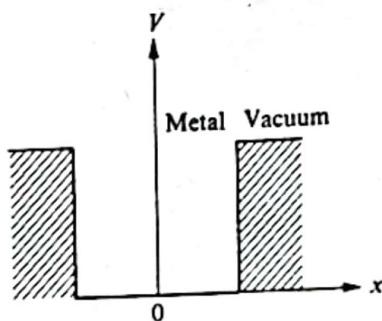


Fig. 4.2 The potential in the free-electron model.

Let us look at the model a little more closely. It is surprising that it should be valid at all, because, at first sight, one expects the conduction electrons to interact with the ions in the background, and also with each other. These interactions are strong, and hence the electrons ought to suffer frequent collisions; a picture of a highly nonideal gas should therefore emerge. Why then does the free-electron model work? The answer to this fundamental question was not known to the workers who first postulated the model. We now know the answer, but since it requires the use of quantum mechanics, we shall postpone the discussion to Chapter 5. Only a brief qualitative statement is offered here.

The reason why the interaction between the ions appears to be weak is as follows. Although the electron does interact with an ion through coulomb attraction, quantum effects introduce an additional *repulsive* potential, which tends to cancel the coulomb attraction. The net potential—known as the *pseudopotential*—turns out to be weak, particularly in the case of alkali metals. Another way of approaching this is to note that, when an electron passes an ion, its velocity

[†] In this chapter we use the symbol N for electron concentration. The symbol n will be reserved for the optical index of refraction, discussed in Section 4.11.

increases rather rapidly in the ion's neighborhood (Fig. 4.3), due to the decrease in the potential. Because of this, the electron spends only a small fraction of its time near the ion, where the potential is strong. Most of the time the electron is far away in a region in which the potential is weak, and this is why the electron behaves like a free particle, to a certain approximation.[†] We shall talk about the electron-ion interaction again in Section 5.3, and the pseudopotential in Section 5.9.

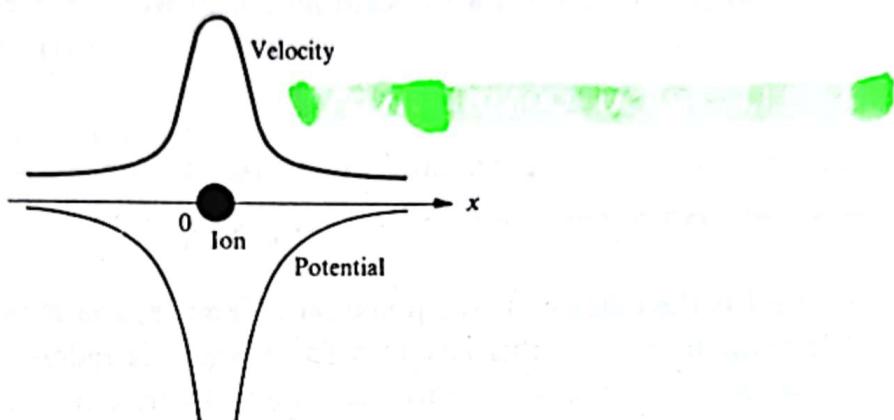


Fig. 4.3 Variation of the local velocity of electrons in space.

We come now to the interaction between the conduction electrons themselves, and the reason for the weakness of this interaction. There are actually two reasons: First, according to the Pauli exclusion principle, electrons of parallel spins tend to stay away from each other. Second, even if their spins are opposite, electrons tend to stay away from each other, in order to minimize the energy of the system. If two electrons come very close to each other, the coulomb potential energy becomes exceedingly large, and this violates the tendency of the electron system to have the lowest possible energy. When these two considerations are carried out mathematically, the following situation results: Each electron is surrounded by a (spherical) region which is deficient of other electrons. This region, called a *hole*, has a radius of about 1 Å (the exact value depends on the concentration of electrons). As an electron moves, its hole—sometimes known as a *Fermi hole*—moves with it. We see now why the interaction between electrons is weak. If we examine the interaction between two particular electrons, we find that other electrons distribute themselves in such a manner that our two electrons are screened from each other. Consequently there is very little interaction between them.

Free-electron gas in metals differs from ordinary gas in some important respects. First, free-electron gas is charged (in ordinary gases the molecules are mostly

[†] Note that the interaction between the electron and ion is very weak when the distance between them is large because the ions are screened by other electrons. This means that the interaction has the form of a short-range *screened* coulomb potential rather than a long-range pure coulomb potential.

neutral). Free-electron gas is thus actually similar to a *plasma*. Second, the concentration of electrons in metals is large: $N \approx 10^{29}$ electrons-m⁻³. By contrast, the ordinary gas has about 10²⁵ molecules-m⁻³. We may thus think of free-electron gas in a metal as a dense plasma.

Our model of the electron (sometimes called the *jellium* model) corresponds to taking metallic positive ions and smearing them uniformly throughout a sample. In this way there is a positive background which is necessary to maintain charge *neutrality*. But, because of the uniform distribution, the ions exert zero field on the electrons; the ions form a uniform *jelly* into which the electrons move.

4.4 ELECTRICAL CONDUCTIVITY

The law of electrical conduction in metals—*Ohm's law*—is

$$I = V/R, \quad (4.2)$$

where I is the current, V the potential difference, and R the resistance of the wire. We want to express this law in a form which is independent of the length and cross section of the wire, since these factors are, after all, irrelevant to the basic physics of conduction. Suppose that L and A are, respectively, the length and cross section of the wire; then

$$J = \frac{I}{A}, \quad \mathcal{E} = \frac{V}{L}, \quad \text{and} \quad R = \frac{L\rho}{A}, \quad (4.3)$$

where J is the *current density* (current per unit area), \mathcal{E} the electric field, and ρ the *electrical resistivity*. The inverse of the resistivity is called the *conductivity*, denoted by σ . That is,

$$\sigma = \frac{1}{\rho}. \quad (4.4)$$

When we substitute (4.3) and (4.4) into (4.2), we arrive at

$$J = \sigma \mathcal{E}, \quad (4.5)$$

which is the form of Ohm's law which we shall use. Since the dimension of ρ is ohm-m, σ has the dimension ohm⁻¹m⁻¹. Now we want to express σ in terms of the microscopic properties pertaining to the conduction electrons.

The current is due to the motion of the conduction electrons under the influence of the field. Because these particles are charged, their motion leads to an electrical current; the motion of neutral particles does not lead to an electrical current. We say that it is the conduction electrons which are responsible for the current because the ions are attached to and vibrate about the lattice sites. They have no net translational motion, and hence do not contribute to the current. Let us now treat the motion of the conduction electrons in an electric field.

Consider one typical electron: The field exerts on the electron a force $-e\mathcal{E}$. There is also a *friction force* due to the collision of the electron with the rest of the medium. Let us assume that this friction force has the form $-m^*v/\tau$, where v is the velocity of the electron and τ is a constant called the *collision time*. Using Newton's law, we have

$$m^* \frac{dv}{dt} = -e\mathcal{E} - m^* \frac{v}{\tau}, \quad (4.6)$$

where m^* is the *effective mass* of the electron.[†] We see that the effect of the collision, as usual in friction or viscous forces, tends to reduce the velocity to zero. We are interested in the steady-state solution; that is, where $dv/dt = 0$. The appropriate solution of (4.6) in this case is

$$v = -\frac{e\tau}{m^*} \mathcal{E}. \quad (4.7)$$

This, then, is the *steady-state velocity* of the electron (in discussions of friction it is usually called the *terminal velocity*). It is opposite to \mathcal{E} because the charge on the electron is negative.

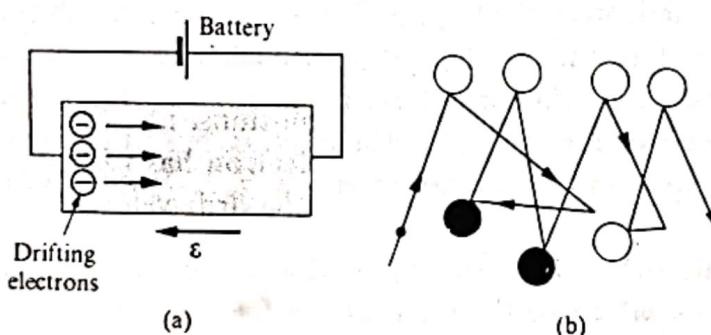


Fig. 4.4 (a) An electric field applied to a metallic wire. (b) Random versus drift motion of electrons. Circles represent scattering centers.

We should make a distinction here between the two different velocities associated with the electron: The velocity appearing in (4.7) is called the *drift velocity*. This is superimposed on a much higher velocity or speed, known as the *random velocity*, due to the random motion of the electron. Just as in an ordinary gas, the electrons have random motion even in the absence of the field. This is due to the fact that the electrons move about and occasionally scatter and change direction. The random motion, which contributes zero current, exists also in the

[†] The effective mass of the electron in a metal, denoted by m^* , is in general different from the free-electron mass, usually denoted by m or m_0 . This difference is due to the interaction of the electron with the lattice, as will be discussed in Section 5.15. The effective masses in various metals are listed in Table 4.1.

presence of a field; but in that case there is an additional net velocity opposite to the field, as given by (4.7). The distinction between random and drift motions is shown in Fig. 4.4. We shall denote the two velocities by v_r and v_d ; it will be shown later that $v_d \ll v_r$.

The current density J can be calculated from (4.7). Since there is a charge ($-Ne$) per unit volume, and since each electron has a drift velocity given by (4.7), it follows that the amount of charge crossing a unit area per unit time is

$$J = (-Ne)v_d = (-Ne) \left(-\frac{e\tau}{m^*} \mathcal{E} \right) = \frac{Ne^2\tau}{m^*} \mathcal{E}. \quad (4.8)$$

The current is *parallel* to the field. Comparing (4.8) with Ohm's law, (4.5), one finds the following expression for the conductivity,

$$\sigma = \frac{Ne^2\tau}{m^*}, \quad (4.9)$$

which is the expression we have been seeking. We see that σ increases as N increases. This is reasonable because, as N (or the concentration) increases, there are more current carriers. The conductivity σ is inversely proportional to m^* , which is again expected, since the larger m^* is, the more sluggish the particle, and the harder it is for it to move. The proportionality to τ follows because τ is actually the time between two consecutive collisions, i.e., the *mean free lifetime*. Therefore the larger τ is, the more time the electron has to be accelerated by the field between collisions, and hence the larger the drift velocity (4.7), and also the larger σ is.

We can evaluate the conductivity σ if we know the quantities on the right of (4.9). We shall take m^* to be the same as the free mass $m_0 = 9.1 \times 10^{-31}$ kg. Then we can calculate N as discussed in Section 4.2. There remains the collision time τ ; this is a quantity which is difficult to calculate from first principles, so we shall postpone discussing it until Section 4.5. For the time being, we can use (4.8) and the measured value of σ to calculate τ . Table 4.1 gives a list of σ , N , τ and other related quantities for various common metals. Note that σ is about 5×10^7 (ohm-m) $^{-1}$. Note in particular that τ has a value of about 10^{-14} s. This is an extremely small time interval on the common time scale, and we shall see later that important conclusions may be drawn from this.

The time τ is also called the *relaxation time*. To see the reason for this, let us suppose that an electric field is applied, long enough for a drift velocity $v_{d,0}$ to be established. Now let the field be suddenly removed at some instant. The drift velocity after this instant is governed by

$$m^* \frac{dv}{dt} = -m^* \frac{v}{\tau},$$

which follows from (4.6) for $\epsilon = 0$. The solution appropriate to the initial condition is now

$$v_d(t) = v_{d,0} e^{-t/\tau}, \quad (4.10)$$

showing that $v_d(t)$ approaches zero exponentially with a characteristic time τ . This behavior is called a *relaxation process*. Since we found above that τ is very short, it follows that $v_d(t)$ relaxes to zero very rapidly.

Table 4.1

Electrical Conductivities and Other Transport Parameters for Metals

Ele- ment	σ , $\text{ohm}^{-1} \text{m}^{-1}$	N , m^{-3}	τ , s	v_F , m/s	l , \AA	E_F , eV	$E_F(\text{obs.})$, eV	m^*/m_0
Li	1.07×10^7	4.6×10^{28}	0.9×10^{-14}	1.3×10^6	110	4.7	3.7	1.2
Na	2.11	2.5	3.1	1.1	350	3.1	2.5	1.2
K	1.39	1.3	4.3	0.85	370	2.1	1.9	1.1
Rb	0.80	1.1	2.75	0.80	220	1.8	—	—
Cs	0.50	0.85	—	0.75	160	1.5	—	—
Cu	5.88	8.45	2.7	1.6	420	7.0	7.0	1.0
Ag	6.21	5.85	4.1	1.4	570	5.5	—	—
Au	4.55	5.90	2.9	1.4	410	5.5	—	—
Zn	1.69	13.10	—	1.82	—	9.4	11.0	0.85
Cd	1.38	9.28	—	1.62	—	7.5	—	—
Hg	0.10	—	—	—	—	—	—	—
Al	3.65	18.06	—	2.02	—	11.6	11.8	—
Ga	0.67	15.30	—	1.91	—	10.3	—	—
In	1.14	11.5	—	1.74	—	8.6	—	—

Values quoted are for metals at room temperature. The concentration is found by using the usual chemical valences. The Fermi velocity v_F and E_F are evaluated by using $m^* = m_0$ and the appropriate equation from Section 4.6. The Fermi energy E_F (observed) is the experimentally determined value as discussed in Chapter 6. The effective mass m^* is determined by using the experimental value E_F (observed) and the relation $E_F = (\hbar^2/2m^*)(3\pi^2N)^{2/3}$, Eq. (4.34).

We shall now rewrite (4.9) in a form which brings out some aspects of the physics more clearly. Since τ is the time between two successive collisions, it may be expressed as

$$\tau = \frac{l}{v_r}, \quad (4.11)$$

where l is the *distance* between two successive collisions and v_r is the random

velocity. In terms of these, σ becomes

$$\sigma = \frac{Ne^2 l}{m^* v_r} \quad (4.12)$$

Let us compare the results of applying this formula to metals and semiconductors. For the former, $\sigma \approx 5 \times 10^7 \text{ (ohm-m)}^{-1}$, as we have seen, while for the latter, $\sigma \approx 1 \text{ (ohm-m)}^{-1}$. The difference can be accounted for by (4.12). First, in semiconductors, $N \approx 10^{20} \text{ m}^{-3}$, as compared with $N \approx 10^{29} \text{ m}^{-3}$ in metals. This reduces σ by a factor of 10^{-9} for semiconductors. Second, v_r in metals is of the order of the *Fermi velocity* (Section 4.7), which is about 10^6 m-s^{-1} , while it is only about 10^4 m-s^{-1} in semiconductors.[†] If we include the effects of both N and v_r , we find the conductivity to be the right order of magnitude for semiconductors.

Let us compare the magnitudes of v_r and v_d . The former has a value of about 10^6 m-s^{-1} ; on the other hand, v_d can be evaluated from (4.7). When we substitute for e , τ , and m^* in (4.7) their values: $e \approx 10^{-19} \text{ coul}$, $\tau = 10^{-14} \text{ s}$, $m^* \approx 10^{-30} \text{ kg}$, and $\mathcal{E} \approx 10 \text{ V/m}$, we find that $v_d \approx 10^{-2} \text{ m-s}^{-1}$. Thus $v_d/v_r \approx 10^{-8}$, a very small ratio indeed.

We can also find the microscopic expression for the joule heat. The power dissipated as joule heat must be equal to the power absorbed by the electron system from the field. Recalling from elementary physics that the power absorbed by a particle from force F is Fv , where v is the velocity of the particles, we see that the power absorbed by the electron system per unit volume is

$$\begin{aligned} P &= NFv_d = N(-e\mathcal{E}) \left(-\frac{e\tau\mathcal{E}}{m^*} \right) \\ &= \frac{Ne^2\tau}{m^*} \mathcal{E}^2. \end{aligned} \quad (4.13)$$

The origin of collision time

We have introduced τ as collision time due to some friction force, the source of which was not discussed. It seems natural to assume that the friction force is caused by the collision of electrons with ions. According to this particular model of collision, an electron, as it moves in the lattice, collides with ions, which has the effect of slowing down the electron's momentum. This model turns out to be untenable because it leads to many points of disagreement with experiment. To cite only one: The mean free path l can be calculated from (4.11). If we substitute the values $\tau \approx 10^{-14} \text{ s}$ and $v_r \approx 10^6 \text{ m-s}^{-1}$, we find that $l \approx 10^{-8} \text{ m} \approx 10^2 \text{ \AA}$. This means that, between two collisions, the electron travels a distance of more than

[†] In semiconductors, random velocity is given by the usual expression $v_r = (3kT/m^*)^{1/2}$ due to thermal motion. If we substitute $T = 300 \text{ K}$ and $m^* = m_0/5$, a typical value for the effective mass in semiconductors, we find that $v_r = 10^4 \text{ m-s}^{-1}$.

20 times the interatomic distance. This is much larger than one would expect if the electron really *did* collide with the ions whenever it passed them. Especially in close-packed structures, in which the atoms are densely packed, it is difficult to see how the electrons could travel so far between collisions.

This paradox can be explained only by the use of quantum concepts. The essence of the argument is as follows: We saw in Section 2.12 that, according to quantum mechanics, an electron has a wave character. The wavelength of the electron in the lattice is given by the deBroglie relation (Section A.1),

$$\lambda = \frac{h}{m^* v_r}. \quad (4.14)$$

It is well known from the theory of wave propagation in discrete structures[†] that, when a wave passes through a periodic lattice, it continues propagating indefinitely without scattering. The effect of the atoms in the lattice is to absorb energy from the wave and radiate it back, so that the net result is that the wave continues without modification in either direction or intensity. The *velocity* of propagation, however, is modified. This is what happens in the case of an electron wave in a regular lattice, except that in this case we are dealing with a matter wave.

We discussed the mathematical reason why a regular lattice does not scatter a wave in some detail in Chapter 2. There we saw that the wave—be it x-ray, neutron, or electron—does not scatter or diffract except when the Bragg condition is satisfied. Save under this special condition, the conduction electron should not be scattered by a regular lattice of ions at all.

There is a familiar example in optics: A light wave traveling in a crystal is not scattered at all. The only effect the crystal has is to introduce the index of refraction n so that the velocity in the medium is c/n . Therefore we see that, if the ions form a perfect lattice, there is no collision at all—that is, $\tau = \infty$ —and hence $\sigma = \infty$, which in turn leads to infinite conductivity. It has been shown, however, that the observed σ is about $10^2 \text{ } \text{\AA}^{-1}$. The finiteness of σ must thus be due to the deviation of the lattice from perfect periodicity; this happens either because of thermal vibration of the ions, or because of the presence of imperfections or foreign impurities, as we shall see in the next section.

4.5 ELECTRICAL RESISTIVITY VERSUS TEMPERATURE

The electrical conductivity of a metal varies with the metal's temperature in a characteristic manner. This variation is usually discussed in terms of the behavior of the resistivity ρ versus T . Figure 4.5 shows the observed curve for Na. At $T \approx 0^\circ\text{K}$, ρ has a small *constant* value; above that, ρ increases with T , slowly at first, but afterward ρ increases linearly with T . The linear behavior continues essen-

[†] See, e.g., L. Brillouin, 1953, *Wave Propagation in Periodic Structures*, New York: Dover Press.

ally until the melting point is reached. This pattern is followed by most metals (except as noted below), and usually room temperature falls into the linear range. The linear behavior is readily verified experimentally, as you may recall from elementary physics.

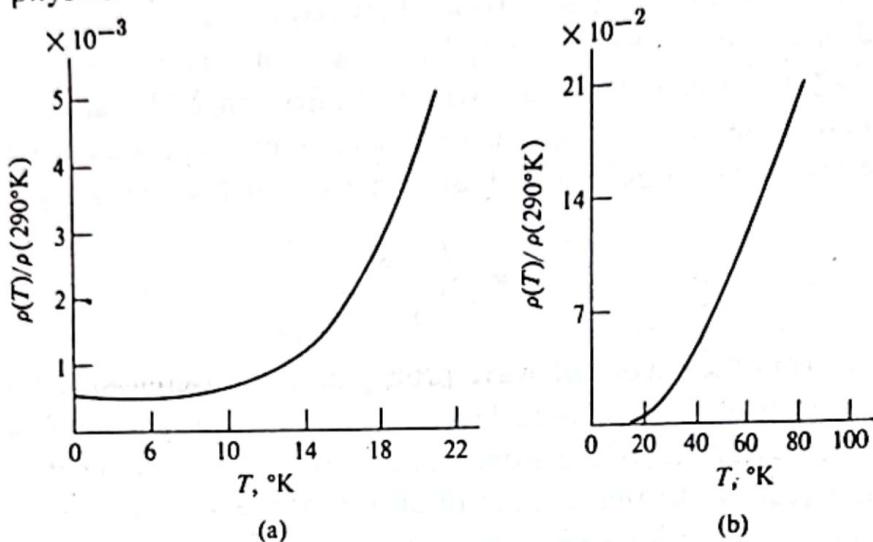


Fig. 4.5 The normalized resistivity $\rho(T)/\rho(290^\circ\text{K})$ versus T for Na in the low-temperature region (a), and at higher temperatures (b). $\rho(290) \approx 2.10 \times 10^{-8} \Omega\text{-m}$.

We want to explain this behavior of ρ in terms of the formulas developed in Section 4.4. Recalling that $\rho = \sigma^{-1}$, and using (4.9), we have

$$\rho = \frac{m^*}{Ne^2} \frac{1}{\tau}. \quad (4.15)$$

We note from the interpretation of τ in the last section that $1/\tau$ is actually equal to the probability of the electron suffering a scattering per unit time. Thus, if $\tau = 10^{-14}\text{s}$, then the electron undergoes 10^{14} collisions in one second. But in Section 4.4 we saw that the electron undergoes a collision only because the lattice is not perfectly regular. We group the deviations from a perfect lattice into two classes.

- 1) Lattice vibrations (phonons) of the ions around their equilibrium position due to thermal excitation of the ions.
- 2) All static imperfections, such as foreign impurities or crystal defects. Of this latter group we shall take foreign impurities as an example. Now the probabilities of electrons being scattered by phonons and by impurities are additive, since these two mechanisms are assumed to act independently. Therefore we may write

$$\frac{1}{\tau} = \frac{1}{\tau_{ph}} + \frac{1}{\tau_i}, \quad (4.16)$$

where the first term on the right is due to phonons and the second is due to

impurities. The former is expected to depend on T and the latter on impurities, but not on T . When (4.16) is substituted into (4.15), we readily find

$$\rho = \rho_i + \rho_{ph}(T) = \frac{m^*}{Ne^2} \frac{1}{\tau_i} + \frac{m^*}{Ne^2} \frac{1}{\tau_{ph}}. \quad (4.17)$$

We note that ρ has split into two terms: a term ρ_i due to scattering by impurities (which is independent of T), called the *residual resistivity*. Added to this is another term $\rho_{ph}(T)$ due to scattering by phonons; hence it is temperature dependent, and is called the *ideal resistivity*, in that it is the resistivity of a pure specimen.

At very low T , scattering by phonons is negligible because the amplitudes of oscillation are very small; in that region $\tau_{ph} \rightarrow \infty$, $\rho_{ph} \rightarrow 0$, and hence $\rho = \rho_i$, a constant. This is in agreement with Fig. 4.5. As T increases, scattering by phonons becomes more effective, and $\rho_{ph}(T)$ increases; this is why ρ increases. When T becomes sufficiently large, scattering by phonons dominates and $\rho \approx \rho_{ph}(T)$. In the high-temperature region, $\rho_{ph}(T)$ increases linearly with T , as we shall shortly show. This is again in agreement with experiment, as shown in Fig. 4.5. The statement that ρ can be split into two parts, one of which is independent of T , is known as the *Matthiessen rule*. This rule is embodied in (4.17).

We expect that ρ_i should increase with impurity concentrations, and indeed it will be shown that for small concentrations ρ_i is proportional to the impurity concentration N_i . We also remark that, for small impurity concentration, $\rho_{ph} \gg \rho_i$, except at very low T . Let us now derive approximate expressions for τ_i and τ_{ph} , using arguments from the kinetic theory of gases. We shall assume, for simplicity, that the collision is of the hard-spheres (billiard-ball) type.

Consider first the collision of electrons with impurities. We write

$$\tau_i = \frac{l_i}{v_r}, \quad (4.18)$$

after (4.11), where l_i is the mean free path for collision with impurities. Given that the *scattering cross section* of an impurity is σ_i —which is the area an impurity atom presents to the incident electron—then, using an argument familiar from the kinetic theory of gases, one may write

$$l_i \sigma_i N_i = 1$$

or

$$l_i = \frac{1}{N_i \sigma_i}. \quad (4.19)$$

It is expected that σ_i is of the same magnitude as the actual geometrical area of the impurity atom. That is, that $\sigma_i \approx 1 \text{ \AA}^2$. (Calculations of the exact value of σ_i require quantum scattering theory.) By substituting from (4.18) and (4.19) into (4.17), one can find ρ_i . One then sees that ρ_i is proportional to N_i , the concentration of impurities.

Calculating τ_{ph} is more difficult, but equations similar to (4.18) and (4.19) will hold. In particular, one may write

$$\tau_{ph} = \frac{1}{N_{ion} \sigma_{ion}}, \quad (4.20)$$

here N_{ion} is the concentration of metallic ions in the lattice and σ_{ion} is the scattering cross section per ion. We should note here that σ_{ion} has no relation to the geometrical cross section of the ion. Rather it is the area presented by the thermally fluctuating ion to the passing electron. Suppose that the distance of deviation from equilibrium is x ; then the average scattering cross section is about

$$\sigma_{ion} \approx \pi \langle x^2 \rangle, \quad (4.21)$$

here $\langle x^2 \rangle$ is the average of x^2 . The value $\langle x^2 \rangle$ can be estimated as follows: since the ion is a harmonic oscillator (Section 3.4), the average of its potential energy is equal to half the total energy. Thus

$$\frac{1}{2} \alpha \langle x^2 \rangle = \langle E \rangle = \frac{\hbar \omega}{e^{\hbar \omega/kT} - 1}, \quad (4.22)$$

here we used the formula for the energy of a quantum oscillator (Section 3.4). The frequency ω is either the Einstein or the Debye frequency, because in this rough argument we can ignore the difference between these two frequencies. We may introduce the Debye temperature θ so that $\hbar \omega = k\theta$. When we make these substitutions into (4.17), we find that $\rho_{ph}(T)$ can be written as

$$\rho_{ph}(T) \propto \left(\frac{\pi \hbar^2}{k \theta M} \right) \frac{1}{e^{\hbar \omega/kT} - 1}, \quad (4.23)$$

here M is the mass of the ion. In the range $T \gg \theta$, this can be written as

$$\rho_{ph}(T) \propto \left(\frac{\pi \hbar^2}{k \theta M} \right) \frac{T}{\theta}, \quad (4.24)$$

which is linear in T , as promised, and in agreement with experiment.

In the low-temperature range, Eq. (4.23) predicts that $\rho_{ph}(T)$ will decrease exponentially as $e^{-\theta/T}$. However, the observed decrease is as T^5 . The reason for this discrepancy is that we used the Einstein model, in which the motion of the neighboring ions was treated independently. When the correlation between ionic motions is taken into account, as in the Debye theory of lattice vibrations, one obtains the T^5 behavior.

Deviations from Matthiessen's rule are often observed, the best known being the Kondo effect. When some impurities of Fe, for example, are dissolved in Cu, ρ does not behave as in Fig. 4.5 at low T . Instead ρ has a minimum at low T . This anomalous behavior is due to an additional scattering of electrons

by the magnetic moments on the impurity centers. Also, deviations from Matthiessen's rule attributable to complications in the band structure of the conduction electrons have been reported. We see from these two examples that the behavior of ρ versus T at very low T may be much more complex than that implied by the simple statement of Matthiessen's rule.

4.6 HEAT CAPACITY OF CONDUCTION ELECTRONS

In the *free-electron model* the conduction electrons are treated as free particles which obey the classical laws of mechanics, electromagnetism, and statistical mechanics. We have already pointed out the difficulty of treating collisions in this model, and also how one must appeal to quantum concepts in order to salvage the model. Another difficulty arises in connection with the heat capacity of the conduction electrons.

Let us calculate the heat capacity per mole for the conduction electrons on the basis of the Drude-Lorentz model. It is well known from the kinetic theory of gases that a free particle in equilibrium at temperature T has an average energy of $\frac{3}{2}kT$. Therefore the average energy per mole is

$$\langle \bar{E} \rangle = N_A (\frac{3}{2}kT) = \frac{3}{2}RT, \quad (4.25)$$

where N_A is Avogadro's number and $R = N_A k$. The electrons' heat capacity $C_e = \partial[\bar{E}]/\partial T$. Therefore

$$C_e = \frac{3}{2}R \approx 3 \text{ cal/mole}^\circ\text{K}. \quad (4.26)$$

The total heat capacity in metals, including phonons, should then be

$$C = C_{ph} + C_e, \quad (4.27)$$

which, at high temperature, has the value

$$C = 3R + \frac{3}{2}R = 4.5R \approx 9 \text{ cal/mole}^\circ\text{K}. \quad (4.28)$$

Experiments on heat capacity in metals show, however, that C is very nearly equal to $3R$ at high T , as is the case for insulators. Accurate measurements in which the contributions of electrons to total heat capacity are isolated show that C_e is smaller than the classical value $\frac{3}{2}R$ by a factor of about 10^{-2} . To explain this discrepancy, we must once again turn to quantum concepts.

The energy of the electron in a metal is quantized according to quantum mechanics. Figure 4.6(a) shows the quantum energy levels. The electrons in the metal occupy these levels. In doing so, they follow a very important quantum principle, the *Pauli exclusion principle*, according to which an energy level can accommodate at most two electrons, one with spin up, and the other with spin down. Thus in filling the energy levels, two electrons occupy the lowest level, two more

the next level, and so forth, until all the electrons in the metal have been accommodated, as shown in Fig. 4.6(a). The energy of the highest occupied level is called the *Fermi energy* (or simply the *Fermi level*). We shall evaluate the Fermi energy in Section 4.7. A typical value for the Fermi energy in metals is about 5 eV.

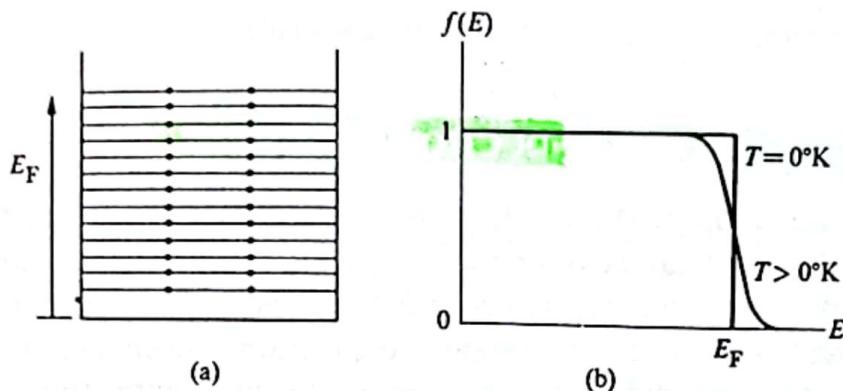


Fig. 4.6 (a) Occupation of energy levels according to the Pauli exclusion principle. (b) The distribution function $f(E)$ versus E , at $T = 0^\circ\text{K}$ and $T > 0^\circ\text{K}$.

The situation described obtains in metals at $T = 0^\circ\text{K}$. Even at the lowest possible temperature, the electron system has a considerable amount of energy, in virtue of the exclusion principle. If it were not for this principle, all the electrons would fall into the lowest level, and the total energy of the system would be negligible. This corresponds to the assertion, usually made in classical mechanics, that as $T \rightarrow 0^\circ\text{K}$ all motion ceases, and the energy vanishes. This assertion clearly does not apply to the conduction electrons.

The distribution of electrons among the levels is usually described by the *distribution function*, $f(E)$, which is defined as the probability that the level E is occupied by an electron. Thus if the level is certainly empty, then $f(E) = 0$, while if it is certainly full, then $f(E) = 1$. In general, $f(E)$ has a value between zero and unity.

It follows from the preceding discussion that the distribution function for electrons at $T = 0^\circ\text{K}$ has the form

$$f(E) = \begin{cases} 1, & E < E_F \\ 0, & E_F < E \end{cases} \quad (4.29)$$

That is, all levels below E_F are completely filled, and all those above E_F are completely empty. This function is plotted in Fig. 4.6(b), which shows the discontinuity at the Fermi energy.

We have thus far restricted our treatment to the temperature at absolute zero. When the system is heated ($T > 0^\circ\text{K}$), thermal energy excites the electrons. But this energy is not shared equally by all the electrons, as would be the case in the classical treatment, because the electrons lying well below the Fermi level E_F cannot absorb energy. If they did so, they would move to a higher level, which would already be occupied, and hence the exclusion principle would be violated.

Recall in this context that the energy which an electron may absorb thermally is of the order kT ($= 0.025$ eV at room temperature), which is much smaller than E_F , this being of the order of 5 eV. Therefore only those electrons close to the Fermi level can be excited, because the levels above E_F are empty, and hence when those electrons move to a higher level there is no violation of the exclusion principle. Thus only these electrons—which are a small fraction of the total number—are capable of being thermally excited, and this explains the low electronic specific heat (or heat capacity).

The distribution function $f(E)$ at temperature $T \neq 0^\circ\text{K}$ is given by

$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}. \quad (4.30)$$

This is known as the *Fermi-Dirac distribution*.[†] This function is also plotted in Fig. 4.6(b), which shows that it is substantially the same as the distribution at $T = 0^\circ\text{K}$, except very close to the Fermi level, where some of the electrons are excited from below E_F to above it. This is, of course, to be expected, in view of the above discussion.[‡]

One can use the distribution function (4.30) to evaluate the thermal energy and hence the heat capacity of the electrons, but this is a fairly tedious undertaking, so instead we shall attempt to obtain a good approximation with a minimum of mathematical effort. Since only electrons within the range kT of the Fermi level are excited, we conclude that only a fraction kT/E_F of the electrons is affected. Therefore the number of electrons excited per mole is about $N_A(kT/E_F)$, and since each electron absorbs an energy kT , on the average, it follows that the thermal energy per mole is given approximately by

$$\bar{E} = \frac{N_A(kT)^2}{E_F},$$

and the specific heat $C_e = \partial\bar{E}/\partial T$ is

$$C_e = 2R \frac{kT}{E_F}. \quad (4.31)$$

We see that the specific heat of the electrons is reduced from its classical value, which is of the order of R , by the factor kT/E_F . For $E_F = 5$ eV and $T = 300^\circ\text{K}$, this

[†] For a derivation see, for example, M. Alonso and E. J. Finn, 1968, *Fundamental University Physics*, Volume III, Reading Mass.: Addison-Wesley.

[‡] Note that, in the energy range far above the Fermi energy, $(E - E_F)/kT \gg 1$, and hence the Fermi-Dirac distribution function has the form $f(E) = e^{E_F/kT} e^{-E/kT} = \text{constant} \times e^{-E/kT}$, which is the classical—or Maxwell-Boltzmann—distribution. Thus in the high energy range, i.e., in the tail of the Fermi-Dirac distribution, electrons may be treated by classical statistical mechanics.

ctor is equal to 1/200. This great reduction is in agreement with experiment, as pointed out previously.

The so-called *Fermi temperature* T_F , which is sometimes used in this context, defined as $E_F = kT_F$, and the specific heat may now be written as

$$C_e = 2R \frac{T}{T_F}.$$

A typical value for T_F , corresponding to $E_F = 5\text{ eV}$, is $60,000^\circ\text{K}$. Thus in order for the specific heat of the electrons in a solid to reach its classical value, the solid must be heated to a temperature comparable to T_F . But this is not possible, of course, as the solid would long since have melted and evaporated! At all practical temperatures, therefore, the specific heat of electrons is far below its classical value.

Another interesting conclusion from (4.31) is that the heat capacity C_e of the electrons is a linear function of temperature. This is unlike the lattice heat capacity C_L , which is constant at high temperature, and proportional to T^3 at low temperature.

An exact evaluation of the electronic heat capacity yields the value

$$C_e = \frac{\pi^2}{2} R \frac{kT}{E_F}, \quad (4.32)$$

which is clearly of the same order of magnitude as the approximate expression (4.31).

7 THE FERMI SURFACE

The electrons in a metal are in a continuous state of random motion. Because these electrons are considered to be free particles, the energy of an electron is entirely kinetic, and one may therefore write

$$E = \frac{1}{2} m^* v^2,$$

where v is the speed of the particle. Now let us introduce the concept of *velocity space*, whose axes are v_x , v_y , and v_z . Each point in this space represents a unique velocity—both in magnitude and direction.

Consider the conduction electrons in this velocity space. These electrons have many different velocities, and since these velocities are random, the points representing them fill the space uniformly, as shown in Fig. 4.7. Note, however, that there is a sphere outside which all points are empty. The radius of this sphere is the *Fermi speed* v_F , which is related to the Fermi energy by the usual relation

$$E_F = \frac{1}{2} m^* v_F^2. \quad (4.33)$$

The reason why all points outside the sphere are empty is that they correspond to energies greater than E_F , which are unoccupied at $T = 0^\circ\text{K}$, as discussed in Section 4.6. All the points inside the sphere are completely full. This sphere is known as the *Fermi sphere*, and its surface as the *Fermi surface*.

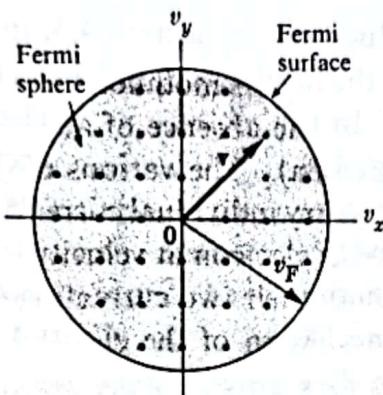


Fig. 4.7 The Fermi surface and the Fermi sphere.

The Fermi surface (FS), which is very significant in many solid-state phenomena—for example, transport properties—is not affected appreciably by temperature. When the temperature is raised, only relatively few electrons are excited from the inside to the outside of the Fermi surface, and these have very little effect, as we have seen. Thus the FS has an independent, permanent identity, and should be regarded as a real physical characteristic of the metal.

The Fermi speed v_F is very large. If we substitute $E_F = 5 \text{ eV}$ in (4.33) and calculate v_F , we find that $v_F = (2E_F/m^*)^{1/2} \simeq (2 \times 5 \times 1.6 \times 10^{-19}/9 \times 10^{-31})^{1/2} \simeq 10^6 \text{ m}\cdot\text{s}^{-1}$, which is about one-hundredth of the speed of light. Thus electrons at the FS are moving very fast. Furthermore, the Fermi speed, like the Fermi surface, is independent of temperature.

The value of the Fermi energy is determined primarily by the electron concentration. The greater the concentration, the higher the topmost energy level required to accommodate all the electrons (refer to Fig. 4.6a), and hence the higher the E_F . Section 5.12 will show that E_F is given by

$$E_F = \frac{\hbar^2}{2m^*} (3\pi^2 N)^{2/3}. \quad (4.34)$$

If one substitutes the typical value $N = 10^{28} \text{ m}^{-3}$, one finds that $E_F \simeq 5 \text{ eV}$, in agreement with our earlier statements. Table 4.1 lists the Fermi energies for various metals.

The Fermi surface will be discussed in much greater detail in Section 5.12, where the interaction of the electrons with the lattice is taken into account. We shall find there that the FS may be distorted from the simple spherical shape

nsidered here, this distortion being engendered by the electron-lattice interaction. For the time being, however, the free-electron model and its FS interaction.

3 ELECTRICAL CONDUCTIVITY; EFFECTS OF THE FERMI SURFACE

We discussed electrical conductivity in Section 4.3, in which we treated electrons on a classical basis. How are the results modified when the FS is taken into account?

Let us refer to Fig. 4.8. In the absence of an electric field, the Fermi sphere is centered at the origin (Fig. 4.8a). The various electrons are all moving—some very high speeds—and they carry individual currents. But the total current of the system is zero, because, for every electron at velocity v there exists another electron with velocity $-v$, and the sum of their two currents is zero. Thus the total current vanishes due to pairwise cancellation of the electron currents.

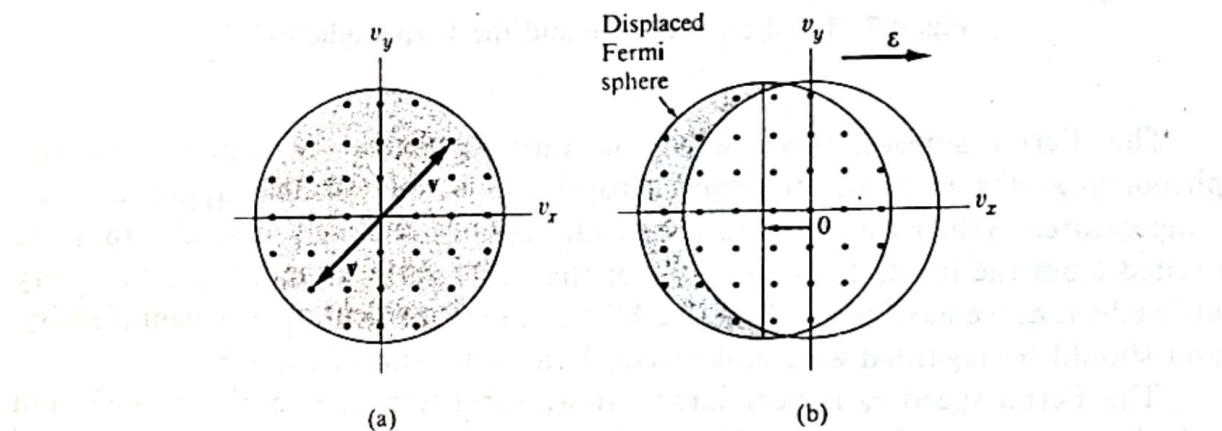


Fig. 4.8 (a) The Fermi sphere at equilibrium. (b) Displacement of the Fermi sphere due to an electric field.

The situation changes when a field is applied. If the field is in the positive v -direction, each electron acquires a drift velocity $v_d = - (e\tau/m^*)\epsilon$, as given by (4.7). Thus the whole Fermi sphere is displaced to the left, as shown in Fig. 4.8(b). Although the displacement is very small, and although the great majority of the electrons still cancel each other pairwise, some electrons—in the shaded crescent in the figure—remain uncompensated. It is these electrons which produce the observed current.

Let us estimate the current density: The fraction of electrons which remain uncompensated is approximately v_d/v_F . The concentration of these electrons is therefore $N(v_d/v_F)$, and since each electron has a velocity of approximately $-v_F$, the current density is given by

$$J \approx -e N(v_d/v_F)(-v_F) = N e v_d,$$

which, on substitution of $v_d = - (e\tau/m^*)\mathcal{E}$, yields

$$J = \frac{N e^2 \tau_F}{m^*} \mathcal{E},$$

where τ_F is the collision time of an electron at the FS. The resulting electrical conductivity is therefore

$$\sigma = \frac{N e^2 \tau_F}{m^*}. \quad (4.35)$$

This is precisely the same as the result obtained classically, except that τ is replaced by τ_F . The expression (4.35), which is only an approximate derivation, can be corroborated by a more detailed and accurate statistical analysis.

The actual picture of electrical conduction is thus quite different from the classical one envisaged in Section 4.4, in which we assumed that the current is carried equally by all electrons, each moving with a very small velocity v_d . The current is, in fact, carried by very few electrons only, all moving at high velocity. Both approaches lead to the same result, but the latter is the more accurate. This can be seen from the fact that only the collision time for electrons at the FS, τ_F , appears in expression (4.35) for σ .

If we substitute $\tau_F = l_F/v_F$ into (4.35), we find that

$$\sigma = \frac{Ne^2 l_F}{m^* v_F}.$$

The only quantity on the right side which depends on temperature is the mean free path l_F . Since $l_F \sim 1/T$ at high temperature, as we saw in Section 4.5, it follows that $\sigma \sim 1/T$ or $\rho \sim T$, in agreement with our previous discussion of electrical resistivity.

The importance of the FS in transport phenomena is now clear. Since the current is transported by electrons lying close to the Fermi surface, these phenomena are very sensitive to the properties, shape, etc., of this surface. The inner electrons are irrelevant so far as conduction processes are concerned.

The fact that essentially the same answer may be obtained classically as quantum mechanically (with proper adjustment of the collision time) encourages us to use the simpler classical procedure. This we shall do wherever feasible in the following sections.

4.9 THERMAL CONDUCTIVITY IN METALS

When the ends of a metallic wire are at different temperatures, heat flows from the hot to the cold end. (Recall our discussion in Section 3.9 on thermal conductivity in insulators.) The basic experimental fact is that the heat current Q —that is,

the amount of thermal energy crossing a unit area per unit time—is proportional to the temperature gradient,

$$Q = -K \frac{dT}{dx},$$

here K is the thermal conductivity. In insulators, heat is carried entirely by phonons, but in metals heat may be transported by both electrons and phonons. The conductivity K is therefore equal to the sum of the two contributions,

$$K = K_e + K_{ph},$$

here K_e and K_{ph} refer to electrons and phonons, respectively. In most metals, the contribution of the electrons greatly exceeds that of the phonons, because of the great concentration of electrons; typically $K_{ph} \approx 10^{-2} K_e$. This being so, the conductivity of the phonons will henceforth be ignored in this section.

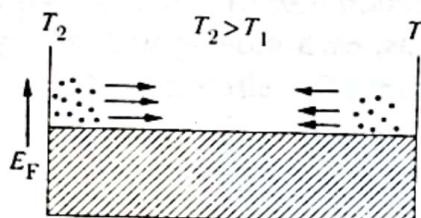


Fig. 4.9 The physical basis for thermal conductivity. Energetic electrons on the left carry net energy to the right.

The physical process by which heat conduction takes place via electrons is illustrated in Fig. 4.9. Electrons at the hot end (to the left) travel in all directions, but a certain fraction travel to the right and carry energy to the cold end. Similarly, a certain fraction of the electrons at the cold end (on the right) travel to the left, and carry energy to the hot end. These oppositely traveling electron currents are equal, but because those at the hot end are more energetic on average than those on the right, a net energy is transported to the right, resulting in a current of heat. Note that heat is transported almost entirely by those electrons near the Fermi levels, because those well below this level cancel each other's contributions. Once more it is seen that the electrons at the FS play a primary role in transport phenomena.

To evaluate the thermal conductivity K quantitatively, we use the formula $K = \frac{1}{3} C_v v l$, used in Section 3.9 in treating heat transport in insulators. We recall that C_v is the specific heat per unit volume, v the speed, and l the mean free path of the particles involved. In the present case, where electrons are involved, C_v is the electronic specific heat and should be substituted from (4.32); also R should be replaced by Nk , since we are dealing here with a unit volume rather than a mole. In addition, v and l should be replaced by v_F and l_F , since only electrons at the

Fermi levels are effective. Thus

$$K = \frac{1}{3} \left(\frac{\pi^2 N k^2 T}{2E_F} \right) v_F l_F.$$

Noting that

$$E_F = \frac{1}{2} m^* v_F^2$$

and that $l_F/v_F = \tau_F$, we can simplify this expression for K to

$$K = \frac{\pi^2 N k^2 T \tau_F}{3m^*}, \quad (4.36)$$

which expresses thermal conductivity in terms of the electronic properties of the metal. Substituting the usual values of the electrons' parameters, one finds $K \approx 50 \text{ cal/m}^\circ\text{K}\cdot\text{s}$. Table 4.2 gives the measured values of K for some metals, and shows that theory is in basic agreement with experiment.

Table 4.2
Thermal Conductivities and Lorenz Numbers (Room Temperature)

Element	Na	Cu	Ag	Au	Al	Cd	Ni	Fe
$K, \text{cal}/\text{m}^\circ\text{K}\cdot\text{s}$	33	94	100	71	50	24	14	16
$L, \text{cal}\cdot\text{ohm}/\text{s}\cdot{}^\circ\text{K}$	5.2×10^{-9}	5.4	5.6	5.9	4.7	6.3	3.7	5.5

Many of the parameters appearing in the expression for K were also included in the expression for electrical conductivity σ . Recalling that $\sigma = Ne^2\tau_F/m^*$, we readily establish that the ratio $K/\sigma T$ is given by

$$L = \frac{1}{3} \left(\frac{\pi k}{e} \right)^2. \quad (4.37)$$

This *Lorenz number* L , because it depends only on the universal constants k and e , should be the same for all metals. Its numerical value is $5.8 \times 10^{-9} \text{ cal}\cdot\text{ohm}/\text{s}\cdot{}^\circ\text{K}^2$. This conclusion suggests that the electrical and thermal conductivities are intimately related, which is to be expected, since both electrical and thermal current are carried by the same agent: electrons.

Table 4.2 lists Lorenz numbers for widely differing metals, and we see that they are close to the predicted values. The fact that the agreement is not exact stems

om (a) the use of the rather simple free-electron model, and (b) the simplified treatment used in calculating the transport coefficients σ and K . A more refined treatment shows that L does indeed depend on the metal under discussion.

10 MOTION IN A MAGNETIC FIELD: CYCLOTRON RESONANCE AND THE HALL EFFECT

The application of a magnetic field to a metal gives rise to several interesting effects arising from the conduction electrons. The *cyclotron resonance* and the *Hall effect* are two which we shall use to investigate the properties of conduction electrons.

Cyclotron resonance

Figure 4.10 illustrates the phenomenon of cyclotron resonance. A magnetic field applied across a metallic slab causes electrons to move in a counterclockwise circular fashion in a plane normal to the field. The frequency of this *cyclotron motion*, known as the *cyclotron frequency*, is given by

$$\omega_c = \frac{eB}{m^*}. \quad (4.38)$$

If we substitute the value of the free-electron mass, we find that

$$\nu_c = \omega_c/2\pi = 2.8B \text{ GHz},$$

where B is in kilogauss. Thus for $B = 1 \text{ kG}$, the cyclotron frequency is $\nu_c = 2.8 \text{ GHz}$, which is in the microwave range.

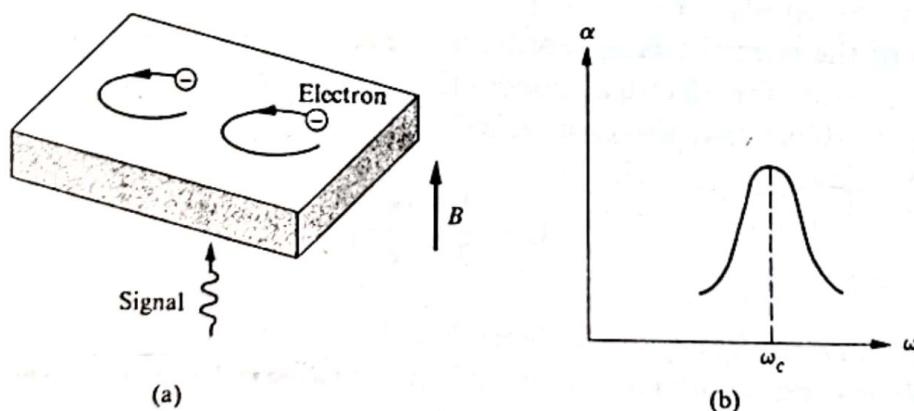


Fig. 4.10 (a) Cyclotron motion. (b) The absorption coefficient α versus ω .

Suppose now that an electromagnetic signal is passed through the slab in a direction parallel to \mathbf{B} , as shown in the figure. The electric field of the signal acts on the electrons, and some of the energy in the signal is absorbed. The rate of

absorption is greatest when the frequency of the signal is exactly equal to the frequency of the cyclotron:

$$\omega = \omega_c. \quad (4.39)$$

This is so because, when this condition holds true, each electron moves synchronously with the wave throughout the cycle, and therefore the absorption continues all through the cycle. Thus Eq. (4.39) is the condition for cyclotron resonance. On the other hand, when Eq. (4.39) is not satisfied, the electron is in phase with the wave through only a part of the cycle, during which time it absorbs energy from the wave. In the remainder of the cycle, the electron is out of phase and returns energy to the wave. The shape of the absorption curve as a function of the frequency is shown in Fig. 4.10(b).†

Cyclotron resonance is commonly used to measure the electron mass in metals and semiconductors. The cyclotron frequency is determined from the absorption curve, and this value is then substituted in (4.38) to evaluate the effective mass. The accuracy with which m^* is determined depends on the accuracy of ω_c and B . One can measure the cyclotron frequency ω_c very accurately, particularly if one uses a laser beam, and therefore the accuracy of measurement of m^* is limited only by the accuracy of measurement of the magnetic field and its homogeneity across the sample.

The Hall effect

The physical process underlying the Hall effect is illustrated in Fig. 4.11. Suppose that an electric current J_x is flowing in a wire in the x -direction, and a magnetic field B_z is applied normal to the wire in the z -direction. We shall show that this leads to an additional electric field, normal to both J_x and B_z , that is, in the y -direction.

To see how this comes about, let us first consider the situation before the magnetic field is introduced. There is an electric current flowing in the positive x -direction, which means that the conduction electrons are drifting with a velocity v in the negative x -direction. When the magnetic field is introduced, the Lorentz force $\mathbf{F} = e(\mathbf{v} \times \mathbf{B})$ causes the electrons to bend downward, as shown in the figure. As a result, electrons accumulate on the lower surface, producing a net negative charge there. Simultaneously a net positive charge appears on the upper surface, because of the deficiency of electrons there. This combination of positive and

† If the peak of the absorption curve is to be clearly discernible, and hence the cyclotron frequency accurately determined, the condition $\omega_c\tau \gg 1$ must be satisfied. This means that the electron can execute many cyclotron cycles during the time it takes to make a single collision. If this condition is not fulfilled, the curve of the collision time is so broad that no unique frequency ω_c is distinguishable.

To make the quantity $\omega_c\tau$ as large as possible, one raises the frequency ω_c by using very high magnetic fields—about 50 kG—and increases the collision time by cooling the sample to low temperatures, e.g., 10^9 K.

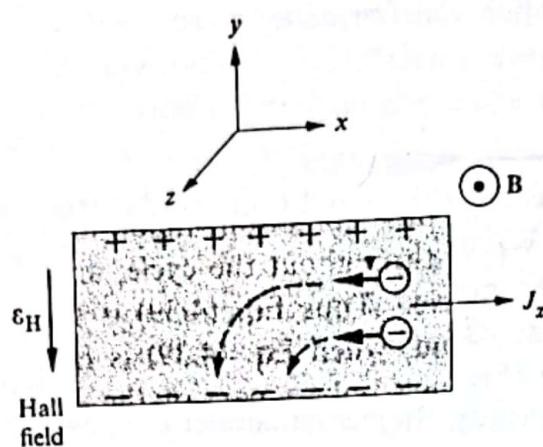


Fig. 4.11 Origin of the Hall field and Hall effect.

negative surface charges creates a downward electric field, which is called the *Hall field*.

Let us evaluate this Hall field. The Lorentz force F_L which produces the charge accumulation in the first place is in the negative y -direction, and has the value

$$F_L = ev_x B,$$

where the sign is properly adjusted so that F_L is negative, in accordance with the figure (recall that v_x , being to the left, is negative). Now the field created by the surface charges produces a force which opposes this Lorentz force. The accumulation process continues until the Hall force completely cancels the Lorentz force. Thus, in the steady state, $F_H = F_L$:

$$-e\mathcal{E}_H = -ev_x B \quad \text{or} \quad \mathcal{E}_H = v_x B,$$

which is the Hall field. It is convenient to express this in terms of measurable quantities, and for this purpose the velocity v_x is expressed in terms of the current density $J_x = N(-e)v_x$. This leads to

$$\mathcal{E}_H = -\frac{1}{Ne} J_x B. \quad (4.40)$$

The Hall field is thus proportional both to the current and to the magnetic field. The proportionality constant—that is, $\mathcal{E}_H/J_x B$ —is known as the *Hall constant*, and is usually denoted by R_H . Therefore

$$R_H = -\frac{1}{Ne}. \quad (4.41)$$

The result (4.41) is a very useful one in practice. Since R_H is inversely proportional to the electron concentration N , it follows that we can determine N by measuring the Hall field. In fact, this is the standard technique for determining electron concentration. The technique is particularly valuable because, apart

from N , the only other quantity on which R_H depends is the charge on the electron, $-e$, which is a fundamental physical constant whose value is known very accurately. Table 4.3 gives Hall constants for some of the common metals.

Table 4.3
Hall Constants (in volt m³/amp weber at Room Temperature)

Li	Na	Cu	Ag	Au	Zn	Cd	Al
-1.7×10^{-10}	-2.50	-0.55	-0.84	-0.72	+0.3	+0.6	-0.30

Another useful feature of the Hall constant is that its sign depends on the sign of the charge of the current carriers. Thus electrons, being negatively charged, lead to a negative Hall constant. By contrast, we shall see in Chapter 5 that the Hall coefficient due to conduction by holes (which are positively charged) is positive.[†] Thus the sign of R_H indicates the sign of the carriers involved, which is very valuable information, particularly in the case of semiconductors. For example, the Hall constants for both Zn and Cd are positive (see Table 4.3), indicating that the current in these substances is carried by holes.

The above analysis shows another interesting aspect of the transport process in the presence of a magnetic field: The current itself, flowing in the x -direction, is uninfluenced by the field. Therefore electrical resistance is independent of magnetic field. This result, even though it is a negative one, is interesting because it is somewhat unexpected. The Lorentz force of the field, which tends to influence J_x , is canceled by the Hall force, so that the electrons flow horizontally through the specimen, oblivious of the field.

4.11 THE AC CONDUCTIVITY AND OPTICAL PROPERTIES

We discussed static electrical conductivity in Section 4.4. Now let us consider electrical conductivity in the presence of an alternating-current field. This is intimately related to the optical properties, as we shall see shortly; the term "optical" here covers the entire frequency range, and is not restricted to the visible region only.

Consider a transverse EM wave, propagating in the x -direction and polarized in the y -direction. Its electric field may thus be expressed as

$$\mathcal{E}_y = \mathcal{E}_0 e^{i(qx - \omega t)}. \quad (4.42)$$

The equation of motion of a conduction electron in the presence of this ac field

[†] These holes, which are different from the Fermi holes mentioned in Section 4.3, will be introduced in Section 5.17, and discussed at length in Chapter 6 on semiconductors.