INTRODUCTION TO THE ELECTRON THEORY OF METALS

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Chapter One

Introduction

1.1 What is the electron theory of metals?

Each element exists as either a solid, or a liquid, or a gas at ambient temperature and pressure. Alloys or compounds can be formed by assembling a mixture of different elements on a common lattice. Typically this is done by melting followed by solidification. Any material is, therefore, composed of a combination of the elements listed in the periodic table, Table 1.1. Among them, we are most interested in solids, which are often divided into metals, semiconductors and insulators. Roughly speaking, a metal represents a material which can conduct electricity well, whereas an insulator is a material which cannot convey a measurable electric current. At this stage, a semiconductor may be simply classified as a material possessing an intermediate character in electrical conduction. Most elements in the periodic table exist as metals and exhibit electrical and magnetic properties unique to each of them. Moreover, we are well aware that the properties of alloys differ from those of their constituent elemental metals. Similarly, semiconductors and insulators consisting of a combination of several elements can also be formed. Therefore, we may say that unique functional materials may well be synthesized in metals, semiconductors and insulators if different elements are ingeniously combined.

A molar quantity of a solid contains as many as 10^{23} atoms. A solid is formed as a result of bonding among such a huge number of atoms. The entities responsible for the bonding are the electrons. The physical and chemical properties of a given solid are decided by how the constituent atoms are bonded through the interaction of their electrons among themselves and with the potentials of the ions. This interaction yields the electronic band structure characteristic of each solid: a semiconductor or an insulator is described by a filled band separated from other bands by an energy gap, and a metal by

Table 1.1. *Periodic table of the elements*

atomic
number
Symbol
atomic
weight
outer electron
configurations
in the ground state

^{1}**H** 1.008 1s																	^{2}**He** 4.003 $1s^2$
^{3}**Li** 6.941 2s	^{4}**Be** 9.012 $2s^2$											^{5}**B** 10.81 $2s^22p$	^{6}**C** 12.01 $2s^22p^2$	^{7}**N** 14.01 $2s^22p^3$	^{8}**O** 16.00 $2s^22p^4$	^{9}**F** 19.00 $2s^22p^5$	^{10}**Ne** 20.18 $2s^22p^6$
^{11}**Na** 22.99 3s	^{12}**Mg** 24.31 $3s^2$											^{13}**Al** 26.98 $3s^23p$	^{14}**Si** 28.09 $3s^23p^2$	^{15}**P** 30.97 $3s^23p^3$	^{16}**S** 32.07 $3s^23p^4$	^{17}**Cl** 35.45 $3s^23p^5$	^{18}**Ar** 39.95 $3s^23p^6$
^{19}**K** 39.10 4s	^{20}**Ca** 40.08 $4s^2$	^{21}**Sc** 44.96 $4s^23d$	^{22}**Ti** 47.88 $4s^23d^2$	^{23}**V** 50.94 $4s^23d^3$	^{24}**Cr** 52.00 $4s3d^5$	^{25}**Mn** 54.94 $4s^23d^5$	^{26}**Fe** 55.85 $4s^23d^6$	^{27}**Co** 58.93 $4s^23d^7$	^{28}**Ni** 58.69 $4s^23d^8$	^{29}**Cu** 63.55 $4s3d^{10}$	^{30}**Zn** 65.39 $4s^23d^{10}$	^{31}**Ga** 69.72 $4s^24p$	^{32}**Ge** 72.59 $4s^24p^2$	^{33}**As** 74.92 $4s^24p^3$	^{34}**Se** 78.96 $4s^24p^4$	^{35}**Br** 79.90 $4s^24p^5$	^{36}**Kr** 83.80 $4s^24p^6$
^{37}**Rb** 85.47 5s	^{38}**Sr** 87.62 $5s^2$	^{39}**Y** 88.91 $5s^24d$	^{40}**Zr** 91.22 $5s^24d^2$	^{41}**Nb** 92.91 $5s4d^4$	^{42}**Mo** 95.94 $5s4d^5$	^{43}**Tc** — $5s4d^6$	^{44}**Ru** 101.1 $5s4d^7$	^{45}**Rh** 102.9 $5s4d^8$	^{46}**Pd** 106.4 $4d^{10}$	^{47}**Ag** 107.9 $5s4d^{10}$	^{48}**Cd** 112.4 $5s^24d^{10}$	^{49}**In** 114.8 $5s^25p$	^{50}**Sn** 118.7 $5s^25p^2$	^{51}**Sb** 121.8 $5s^25p^3$	^{52}**Te** 127.6 $5s^25p^4$	^{53}**I** 126.9 $5s^25p^5$	^{54}**Xe** 131.3 $5s^25p^6$
^{55}**Cs** 132.9 6s	^{56}**Ba** 137.3 $6s^2$	Lantha-nide	^{72}**Hf** 178.5 $6s^25d^24f^{14}$	^{73}**Ta** 180.9 $6s^25d^3$	^{74}**W** 183.9 $6s^25d^4$	^{75}**Re** 186.2 $6s^25d^5$	^{76}**Os** 190.2 $6s^25d^6$	^{77}**Ir** 192.2 $5d^9$	^{78}**Pt** 195.1 $6s5d^9$	^{79}**Au** 197.0 $6s5d^{10}$	^{80}**Hg** 200.6 $6s^25d^{10}$	^{81}**Tl** 204.4 $6s^26p$	^{82}**Pb** 207.2 $6s^26p^2$	^{83}**Bi** 209.0 $6s^26p^3$	^{84}**Po** — $6s^26p^4$	^{85}**At** — $6s^26p^5$	^{86}**Rn** — $6s^26p^6$
^{87}**Fr** — 7s	^{88}**Ra** 226.0 $7s^2$	Acti-nide															

Lantha-nide	^{57}**La** 138.9 $6s^25d$	^{58}**Ce** 140.1 $6s^24f^2$	^{59}**Pr** 140.9 $6s^24f^3$	^{60}**Nd** 144.2 $6s^24f^4$	^{61}**Pm** — $6s^24f^5$	^{62}**Sm** 150.4 $6s^24f^6$	^{63}**Eu** 152.0 $6s^24f^7$	^{64}**Gd** 157.3 $6s^25d4f^7$	^{65}**Tb** 158.9 $6s^25d4f^8$	^{66}**Dy** 162.5 $6s^24f^{10}$	^{67}**Ho** 164.9 $6s^24f^{11}$	^{68}**Er** 167.3 $6s^24f^{12}$	^{69}**Tm** 168.9 $6s^24f^{13}$	^{70}**Yb** 173.0 $6s^24f^{14}$	^{71}**Lu** 175.0 $6s^25d4f^{14}$
Acti-nide	^{89}**Ac** 227.0 $7s^26d$	^{90}**Th** 232.0 $7s^26d^2$	^{91}**Pa** 231.0 $7s^26d5f^2$	^{92}**U** 238.0 $7s^26d5f^3$	^{93}**Np** 237.0 $7s^25f^5$	^{94}**Pu** — $7s^25f^6$	^{95}**Am** — $7s^25f^7$	^{96}**Cm** — $7s^26d5f^7$	^{97}**Bk** —	^{98}**Cf** —	^{99}**Es** —	^{100}**Fm** —	^{101}**Md** —	^{102}**No** —	^{103}**Lr** —

overlapping continuous bands. The resulting electronic structure affects significantly the observed electron transport phenomena. The electron theory of metals in the present book covers properties of electrons responsible for the bonding of solids and electron transport properties manifested in the presence of external fields or a temperature gradient.

Studies of the electron theory of metals are also important from the point of view of application-oriented research and play a vital role in the development of new functional materials. Recent progress in semiconducting devices like the IC (Integrated Circuit) or LSI (Large Scale Integrated circuit), as well as developments in magnetic and superconducting materials, certainly owe much to the successful application of the electron theory of metals. As another unique example, we may refer to amorphous metals and semiconductors, which are known as non-periodic solids having no long-range order in their atomic arrangement. Amorphous Si is now widely used as a solar-operated battery for small calculators.

It may be worthwhile mentioning what prior fundamental knowledge is required to read this book. The reader is assumed to have taken an elementary course of quantum mechanics. We use in this text terminologies such as the wave function, the uncertainty principle, the Pauli exclusion principle, the perturbation theory etc., without explanation. In addition, the reader is expected to have learned the elementary principles of classical mechanics and electromagnetic dynamics.

The units employed in the present book are mostly those of the SI system, but CGS units are often conventionally used, particularly in tables and figures. Practical units are also employed. For example, the resistivity is expressed in units of Ω-cm which is a combination of CGS and SI units. Important units-dependent equations are shown in both SI and CGS units.

1.2 Historical survey of the electron theory of metals

In this section, the reader is expected to grasp only the main historical landmarks of the subject without going into details. The electron theory of metals has developed along with the development of quantum mechanics. In 1901, Planck [1][†] introduced the concept of discrete energy quanta, of magnitude $h\nu$, in the theory of a "black-body" radiation, to eliminate deficiencies of the classical Rayleigh and Wien approaches. Here h is called the Planck constant and ν is the frequency of the electromagnetic radiation expressed as the ratio of the speed of light c over its wavelength λ. In 1905, Einstein [2] explained the

---

[†] Numbers in square brackets are references (see end of book, p. 569).

photoelectric effect (generation of current by irradiation) by making assumptions similar to those of Planck. He assumed the incident light to be made up of energy portions (or “photons” as named later) having discrete energies in multiples of $h\nu$ but that it still behaves like waves with the corresponding frequency. The assumption about a relationship between wave-like and particle-like behavior of light had not been easily accepted at that time.

In 1913, Bohr [3] proposed the electron shell model for the hydrogen atom. He assumed that an electron situated in the field of a positive nucleus was restricted to only certain allowed orbits and that it could “fall” from one orbit to another thereby emitting a quantity of radiation with an energy equal to the difference between the energies of the two orbits. In 1914, Franck and Hertz [4] found that electrons in mercury vapor accelerated by an electric field would cause emission of monochromatic radiation with the wavelength 253.6 nm only when their energy exceeds 4.9 eV. This was taken as a demonstration for the correctness of Bohr’s postulate.[1]

There is, however, a difficulty in the semiclassical theory of an atom proposed by Bohr. According to the classical theory, an electron revolving round a nucleus would lose its energy by emitting radiation and eventually spiral into the nucleus. An enormous amount of effort was expended to resolve this paradox in the period of time between 1913 and 1926, when the quantum mechanical theory became ultimately established. In 1923, Compton [5] discovered that x-rays scattered from a light material such as graphite contained a wavelength component longer than that of the incident beam. A shift of wavelength can be precisely explained by considering the conservation of energy and momentum between the x-ray photons and the freely moving electrons in the solid. This clearly demonstrated that electromagnetic radiation treated as particles can impart momenta to particles of matter and it created a need for constructing a theory compatible with the dual nature of radiation having both wave and particle properties.

In 1925, Pauli [6] postulated a simple sorting-out principle by thoroughly studying a vast amount of spectroscopic data including those associated with the Zeeman effect described below. Pauli found the reason for Bohr’s assignment of electrons to the various shells around the nuclei for different elements in the periodic table. Pauli’s conclusion, which is now known as the “exclusion principle”, states that not more than two electrons in a system (such as an atom) should exist in the same quantum state. This became an important basis

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[1] Radiation with $\lambda = 253.6$ nm is emitted upon the transition from the 6s6p $^3P_1$ excited state to the $6s^2$ $^1S_0$ ground state in mercury. According to Bohr’s postulate, some excited atoms would fall into the ground state thereby emitting radiation with the wavelength $\lambda = 253.6$ nm. Insertion of $\lambda = 253.6$ nm into $\Delta E = hc/\lambda$ exactly yields the excitation energy of 4.9 eV.

in the construction of quantum mechanics. Another important idea was set forth by de Broglie [7] in 1924. He suggested that particles of matter such as electrons, might also possess wave-like characteristics, so that they would also exhibit a dual nature. The de Broglie relationship is expressed as $\lambda = h/p = h/m\mathrm{v}$, where p is the momentum of the particle and λ is the wavelength. A wavelength is best associated with a wave-like behavior and a momentum is best associated with a particle-like behavior. According to this hypothesis, electrons should exhibit a wave-like nature. Indeed, Davisson and Germer [8] discovered in 1927 that accelerated electrons are diffracted by a Ni crystal in a similar manner to x-rays. The formulation of quantum mechanics was completed in 1925 by Heisenberg [9]. Our familiar Schrödinger equation was established in 1926 [10].

The beginning of the electron theory of metals can be dated back to the works of Zeeman [11] and J. J. Thomson [12] in 1897. Zeeman studied the possible effect of a magnetic field on radiation emitted from a flame of sodium placed between the poles of an electromagnet. He discovered that spectral lines became split into separate components under a strong field. He supposed that light is emitted as a result of an electric charge, really an electron, vibrating in a simple harmonic motion within an atom and could determine from this model the ratio of the charge e to the mass m of a charged particle.

At nearly the same time, J. J. Thomson demonstrated that "cathode rays" in a discharge tube can be treated as particles with a negative charge, and he could independently determine the ratio $(-e)/m$. Soon, the actual charge $(-e)$ was separately determined and, as a result, the electron mass calculated from the ratio $(-e)/m$ turned out to be extremely small compared with that of an atom. In this way, it had been established by 1900 that the negatively charged particles of electricity, which are now known as electrons, are the constituent parts of all atoms and are responsible for the emission of electromagnetic radiation when atoms become excited and their electrons change orbital positions.

The classical theory of metallic conductivity was presented by Drude [13] in 1900 and was elaborated in more detail by Lorentz [14] originally in 1905. Drude applied the kinetic theory of gases to the freely moving electrons in a metal by assuming that there exist charged carriers moving about between the ions with a given velocity and that they collide with one other in the same manner as do molecules in a gas. He obtained the electrical conductivity expression $\sigma = ne^2\tau/m$, which is still used as a standard formula. Here, n is the number of electrons per unit volume and τ is called the relaxation time which roughly corresponds to the mean time interval between successive collisions of the electron with ions. He also calculated the thermal conductivity in the same manner and successfully provided the theoretical basis for the Wiedemann–Frantz law already established in 1853. It states that the ratio of the electrical and thermal conductivities of any metal is a universal constant at a given temperature.

Lorentz later reinvestigated the Drude theory in a more rigorous manner by applying Maxwell–Boltzmann statistics to describe the velocities of the electrons. However, a serious difficulty was encountered in the theory. If the Boltzmann equipartition law $\frac{1}{2}m\mathrm{v}^2=\frac{3}{2}k_BT$ is applied to the electron gas, one immediately finds the velocity of the electron to change as $\sqrt{T}$. According to the Drude model, the mean free path is obviously temperature independent, since it is calculated from the scattering cross-section of rigid ions. This results in a resistivity proportional to $\sqrt{T}$, provided that the number of electrons per unit volume n is temperature independent.[2] However, people at that time had been well aware that the resistivity of typical metals increases linearly with increasing temperature well above room temperature. In order to be consistent with the equipartition law, one had to assume n to change as $1/\sqrt{T}$ in metals. This was not physically accepted.

The application of the equipartition law to the electron system was apparently the source of the problem. Indeed, the true mean free path of electrons is found to be as long as 20 nm for pure Cu even at room temperature (see Section 10.2).[3] Another serious difficulty had been realized in the application of the Boltzmann equipartition law to the calculation of the specific heat of free electrons, which resulted in a value of $\frac{3}{2}R$. The well-known Dulong–Petit law holds well even for metals in which free electrons are definitely present. This means that the additional specific heat of $\frac{3}{2}R$ is somehow missing experimentally. We had to wait for the establishment of quantum mechanics to resolve the failure of the Boltzmann equipartition law when applied to the electron gas.

Quantum mechanics imposes specific restrictions on the behavior of electron particles. The Heisenberg uncertainty principle [15] does not permit an exact knowledge of both the position and the momentum of a particle and, as a result, particles obeying the quantum mechanics must be indistinguishable. In 1926, Fermi [16] and Dirac [17] independently derived a new form of statistical mechanics based on the Pauli exclusion principle. In 1927, Pauli [18] applied the newly derived Fermi–Dirac statistics to the calculation of the paramagnetism of a free-electron gas.

In 1928, Sommerfeld [19] applied the quantum mechanical treatment to the electron gas in a metal. He retained the concept of a free electron gas originally introduced by Drude and Lorentz, but applied to it the quantum mechanics

---

[2] The resistivity ρ is given by $\rho=m\mathrm{v}/n(-e)^2\Lambda$, where m is the mass of electron, v is its velocity, n is the number of electrons per unit volume, Λ is the mean free path for the electron and $(-e)$ is the electronic charge (see Section 10.2).

[3] By applying quantum statistics to the electron gas, we will find (in Section 10.2) the true electron velocity responsible for electron conduction in typical metals to be of the order of 10^6 m/s and temperature independent. Instead, the mean free path is shown to be temperature dependent.

coupled with the Fermi–Dirac statistics. The specific heat, the thermionic emission, the electrical and thermal conductivities, the magnetoresistance and the Hall effect were calculated quite satisfactorily by replacing the ionic potentials with a constant averaged potential equal to zero. The Sommerfeld free-electron model could successfully remove the difficulty associated with the electronic specific heat derived from the equipartition law.

The Sommerfeld model was, however, unable to answer why the mean free path of electrons reaches 20 nm in a good conducting metal like silver at room temperature. Indeed, electrons in a metal are moving in the presence of strong Coulomb potentials due to ions. Therefore the success based on the concept of free-electron behavior was received at that time with a great deal of surprise. The ionic potential is periodically arranged in a crystal. In 1928, Bloch [20] showed that the wave function of a conduction electron in the periodic potential can be described in the form of a plane wave modulated by a periodic function with the period of the lattice, no matter how strong the ionic potential. The wave function is called the Bloch wave. The Bloch theorem provided the basis for the electrical resistivity; the entity that is responsible for the scattering of electrons is not the strong ionic potential itself but the deviation from its periodicity. Based on the Bloch theorem, Wilson [21] in 1931 was able to describe a band theory, which embraces metals, semiconductors and insulators. The main frame of the electron theory of metals had been matured by about the middle of the 1930s. We can see it by reading the well-known textbooks by Mott and Jones [22] and Wilson [23] published in 1936.

Before ending this section, the most notable achievements since the 1940s in the field of the electron theory of metals may be briefly mentioned. Bardeen and Brattain invented the point-contact transistor in 1948–49 [24]. For this achievement, the Nobel prize was awarded to Bardeen, Brattain and Shockley in 1956. Superconductivity is a phenomenon in which the electrical resistivity suddenly drops to zero at its transition temperature T_c. The theory of superconductivity was established in 1957 by Bardeen, Cooper and Schrieffer [25]. The so called BCS theory has been recognized as one of the greatest accomplishments in the electron theory of metals since the advent of the Sommerfeld free-electron theory. Naturally, the higher the superconducting transition temperature, the more likely are possible applications. A maximum superconducting transition temperature had been thought to be no greater than 30–40 K within the framework of the BCS theory. However, a new material, which undergoes the superconducting transition above 30 K, was discovered in 1986 [26] and has received intense attention from both fundamental and practical points of view. This was not an ordinary metallic alloy but a cuprate oxide with a complex crystal structure. More new superconductors in this family have been discovered successively and the superconducting transition temperature T_c has increased to be above 90 K in 1987, above 110 K in 1988 and almost 140 K in 1996. The electronic properties manifested by these superconducting oxides have become one of the most exciting and challenging topics in the field of the electron theory of metals.

Originally, the electron theory of metals was constructed for crystals where the existence of a periodic potential was presupposed. Subsequently, an electron theory treatment of a disordered system, where the periodicity of the ionic potentials is heavily distorted, was also recognized to be significantly important. Liquid metals are typical of such disordered systems. More recently, amorphous metals and semiconductors have received considerable attention not only from the viewpoint of fundamental physics but also from many possible practical applications. In addition to these disordered materials, a non-periodic yet highly ordered material known as a quasicrystal was discovered by Shechtman *et al.* in 1984 [27]. The icosahedral quasicrystal is now known to possess two-, three- and five-fold rotational symmetry which is incompatible with the translational symmetry characteristic of an ordinary crystal. The electron theory should be extended to these non-periodic materials and be cast into a more universal theory.

1.3 Outline of this book

Chapters 2 and 3 are devoted to the description of the Sommerfeld free-electron theory. The free-electron model and the concept of the Fermi surface are discussed in Chapter 2. The Fermi–Dirac distribution function is introduced in Chapter 3 and is applied to calculate the electronic specific heat and the thermionic emission. Pauli paramagnetism is also discussed as another example of the application of the Fermi–Dirac distribution function.

Before discussing the motion of electrons in a periodic lattice, we have to study how the periodic lattice can be described in both real and reciprocal space. Fundamental properties associated with both the periodic lattice and lattice vibrations in both real and reciprocal space are dealt with in Chapter 4. In Chapter 5, the Bloch theorem is introduced and then the energy spectrum of conduction electrons in a periodic lattice potential is given in the nearly-free-electron approximation. The mechanism for the formation of an energy gap and its relation to Bragg scattering are described. The concept of the Brillouin zone and its construction are then shown. The Fermi surface and its interaction with the Brillouin zone are considered and the definitions of a metal, a semiconductor and an insulator are given.

In Chapter 6, the Fermi surfaces and the Brillouin zones in elemental metals and semimetals in the periodic table are presented. The reader will discover how the Fermi surface–Brillouin zone interaction in an individual metal results in its own unique electronic band structure. In Chapter 7, the experimental techniques and the principles involved in determining the Fermi surface of metals are introduced. The behavior of conduction electrons in a magnetic field is also treated in this chapter. In Chapter 8, electronic band structure calculation techniques are introduced. The electron theory in alloys is treated in Chapter 9.

Transport phenomena of electrons in crystalline metals are discussed in both Chapters 10 and 11. The derivation of the Boltzmann transport equation and its application to the electrical conductivity are discussed in Chapter 10. In Chapter 11, other transport properties including thermal conductivity, thermoelectric power, Hall coefficient and optical properties are discussed within the framework of the Boltzmann transport equation. At the end of Chapter 11, the basic concept of the Kubo formula is introduced. Superconducting phenomena are presented in Chapter 12, including the introduction of basic theories such as the London theory and BCS theory. The superconducting properties of high-T_c-superconducting materials are also briefly discussed. In Chapter 13, we focus on the electronic structure and electron transport phenomena in magnetic metals and alloys. For example, the resistivity minimum phenomenon known as the Kondo effect, which is observed when a very small amount of magnetic impurities is dissolved in a non-magnetic metal, is described.

The chapters up to 13 are based on the one-electron approximation. But its failure has been recognized to be crucial in the high-T_c-superconducting cuprate oxides and related materials. The materials in this family have been referred to as strongly correlated electron systems. The electronic structure and electron transport properties of a strongly correlated electron system have been studied extensively in the last decade. Its brief outline is, therefore, introduced in Chapter 14. Finally, the electron theory of non-periodic systems, including liquid metals, amorphous metals and quasicrystals is discussed in Chapter 15.

Exercises are provided at the end of most chapters. The reader is asked to solve them since this will certainly assist in the understanding of the chapter content and ideas. Hints and answers are given at the end of the book. References pertinent to each chapter are listed at the end of the book. Several modern textbooks on solid state physics that include the electron theory of metals are also listed [28–32].