SEMI-CONDUCTORS

D. A. WRIGHT

METHUEN'S MONOGRAPHS ON PHYSICAL SUBJECTS

SEMI-CONDUCTORS

by

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PREFACE

THIS book gives an elementary account of the properties of semi-conductors. It is especially concerned with the theory of electron flow in them, and across the boundary between them and either a metal or a vacuum. Much of this theory has been available only in advanced texts or in original papers, and it is hoped that an elementary treatment will be of assistance to students of the electron physics of solids. Only brief reference is made to practical applications and experimental results, as the main interest is in the basic theory.

I am grateful to numerous members of the staff of these Laboratories for assistance with the preparation of this book. In particular, I wish to express my gratitude to Mr. V. J. Francis for reading the manuscript and making suggestions for its improvement, and also to my wife for her assistance in its preparation.

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CHAPTER I

ELECTRONS AND METALS

1. Introduction.—Before proceeding to a discussion of non-metallic solids, it will be necessary to survey briefly the elementary treatment of metals, with special reference to those properties which determine electron flow in the solid and across boundaries between different solids or between a solid and a vacuum. The results of this treatment of the metallic case will be required in deriving the corresponding properties of semi-conductors, and comparison of the results in the two cases will be of interest. It is necessary first to introduce the conception of the energy levels of electrons in a solid, which is invoked continuously in the remainder of the book.

2. Potential Energy of Electrons in a Solid.—When considering the motion of electrons, both in a solid and when escaping from its surface, it is convenient to draw potential-energy diagrams, since the motion of the electrons can be regarded to a first approximation as that of particles in a conservative field of force. A simple case to consider by way of introduction is that of a pendulum bob, in which the potential energy V varies with displacement as in Fig. 1. A particle with total energy H_1 will have potential energy H_1 and kinetic energy zero when the displacement is OB. The kinetic energy will have its maximum value H_1 at zero displacement, and intermediately the potential energy at displacement OA is given by AP. The motion is restricted to that region in which the potential energy V is less than or equal to the total energy H.

It is known experimentally that in order to liberate electrons from a solid, energy must be provided, for example, by heating, by incident radiation, or by bombardment with electrons or other particles. A solid can therefore be represented by a potential-energy diagram as in Fig. 2, in which O is the potential-energy level outside the solid, and A is the corresponding lower level for an electron

in the solid. Thus, when the electron is regarded as a particle in classical mechanics, it will remain in motion inside the solid when its kinetic energy is in the range from zero to AO, for example, if it is AB. If, however, an electron has kinetic energy AC, it can escape from the solid, and outside the solid it will have kinetic energy OC. At room temperature in the dark, very few electrons have total energy greater than AO in any solid, but the number

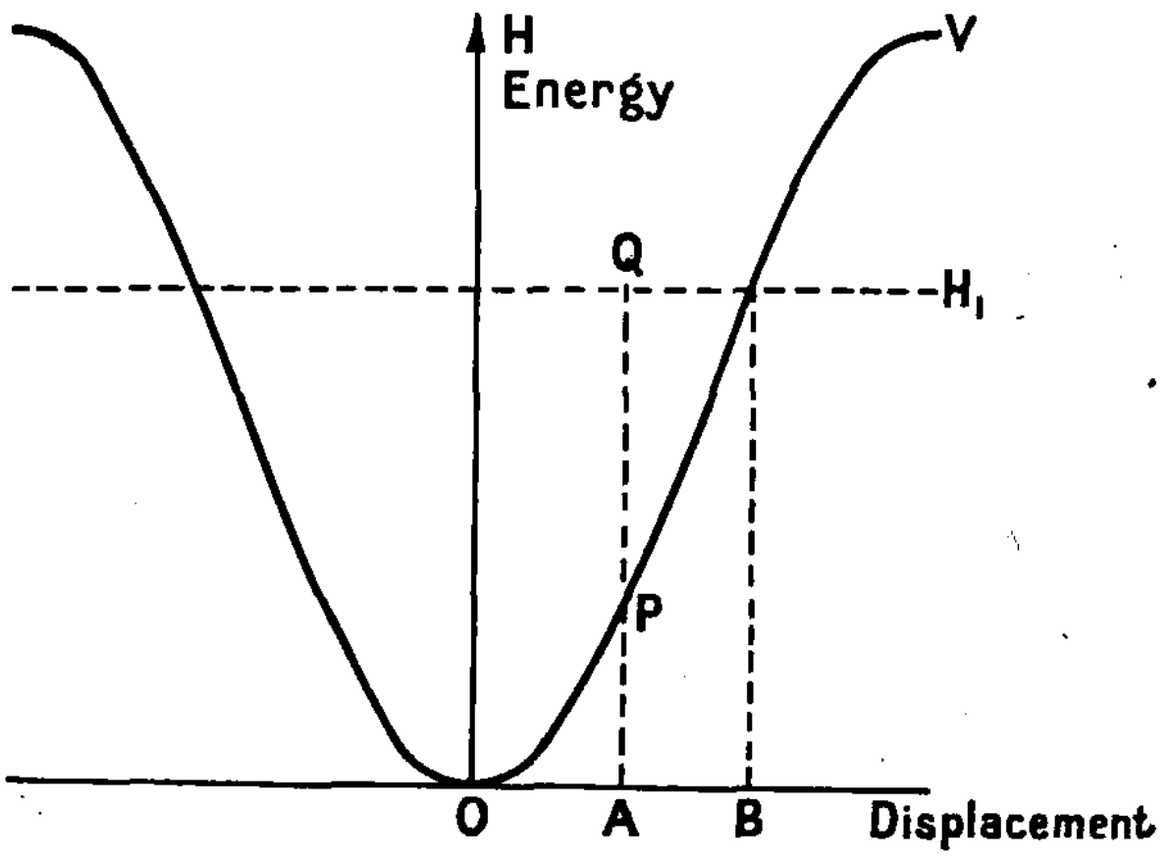

FIG. 1.—Energy of an oscillating pendulum bob

increases with temperature, leading to thermionic emission, while incident light or particles can interact with an electron of kinetic energy AB, increasing it to AC, and so permitting the escape of the electron. This corresponds with photo-electric emission in the case of incident radiation and secondary emission in the case of incident particles.

In considering the behaviour of electrons in a solid in greater detail, it is necessary to have information concerning the number of electrons in motion and the way in which their energies are distributed. In the case of a metal, the simplest assumption is that the metal atoms

arranged in the crystal lattice lose their valency electrons, in the sense that these electrons do not remain attached to particular atoms, but are free to wander in the crystal. If the field of the positive ions is smoothed out, and its local very violent fluctuations are disregarded, the electrons can be regarded as completely free, and can be considered as an ' electron gas '. Since the total field on one electron is that due to the N positive ions in the crystal and the N-1 other electrons, this smoothing out gives a good first approximation. Since there are one or more valency electrons per atom, there will be of the order 10^{22} free electrons per cm.^{3} in the crystal. Their energy distribu-

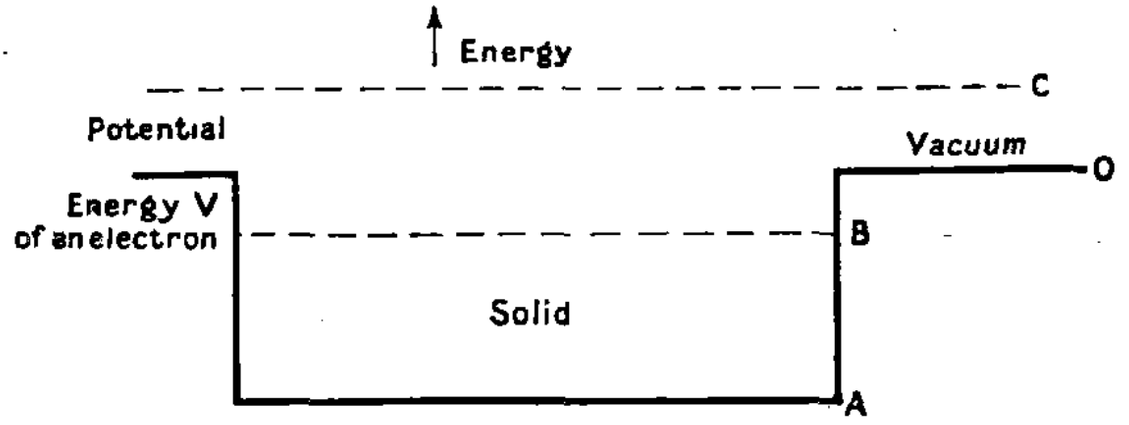

FIG. 2.—Representation of a solid

tion will be determined by application of quantum theory and the exclusion principle. The states of motion in which electrons can exist correspond with discrete energy levels as in a single atom, but the levels are very close together. Nevertheless, the exclusion principle applies, and no more than two electrons (of opposite spins) can be in exactly the same energy state. In applying the quantum rules, we are departing from the conception of an electron as a particle in classical mechanics, and are using the consequences of the wave picture which will be referred to again below. The consequence of the exclusion principle is that even at the absolute zero of temperature, energy levels are occupied by two electrons each, from the zero of kinetic energy to some value W, which is typical of the particular metal. When the temperature is raised, it is only possible for electrons in the highest occupied levels to gain energy until they occupy higher levels,

which were unoccupied at zero temperature. Thus only a small proportion of the total free electrons, the fastest-moving ones, gain energy when the temperature is raised.

3. Fermi–Dirac Statistics.—The energy distribution described above is described mathematically by the Fermi–Dirac statistics, which are based on the exclusion principle and on the indistinguishability of electrons.[1] The result is

$$\delta n_E = \frac{4\pi(2m)^{3/2}}{h^3} \frac{E^{1/2}\delta E}{e^{E-W/kT} + 1} \quad . \quad . \quad . \quad (1)$$

where

δn_E is the number of electrons per cm.^{3} with energy between E and E + δE,
m is the mass of the electron = 9·107 10^{-28} gm.
h is Planck's constant = 6·624 10^{-27} ergs/sec.
e is the base of natural logarithms = 2·718.
k is Boltzmann's constant = 1·381 10^{-16} ergs/degree.
T is the absolute temperature in ° K.
W is an energy which, as will appear below, can be identified with the energy W in Figs. 3 and 4.

This distribution can also be expressed in terms of momentum p, giving δn_p, the number of electrons with momentum between p and $p + \delta p$, as

$$\delta n_p = \frac{8\pi}{h^3} \frac{p^2\delta p}{e^{E-W/kT} + 1} \quad . \quad . \quad . \quad (2)$$

It is clear that when T is zero, the value of δn_E in (1) becomes zero when $E > W$, and has the value $\frac{4\pi}{3}\frac{(2m)^{3/2}}{h^3} E^{1/2}\delta E$ when $E < W$. W is therefore the limiting value of the energy, which is not exceeded at zero temperature. The distribution function therefore follows a half-power law, until $E = W$, when it falls to zero, as in Fig. 3. At a higher temperature, the function follows the dotted curve, showing that a few electrons have energy greater than W.

If the number of electrons is N/cm.^{3}, the fitting in of

this density of electrons into the available number of energy states gives for the height of the Fermi level:

$$W = \frac{h^2}{2m}\left(\frac{3N}{8\pi}\right)^{2/3} \quad . \quad . \quad . \quad . \quad (3)$$

It is convenient here to introduce the electron volt as a unit of energy. It is the energy acquired by an electron in falling through a potential difference of 1 volt, and has the value $1{\cdot}602\ 10^{-12}$ erg. We find that when $N = 10^{21}$, W is 0·38 eV., and when $N = 10^{23}$, W is 8·2 eV. Thus for different metals, W is of the order of a few electron volts, and varies with the atomic spacing and valency.

It is important to note that when E is large compared with W, the distribution more nearly approaches the Maxwellian one, which would apply to classical particles. Thus in this case (1) becomes

$$\delta n_E = \frac{4(2\pi m)^{3/2}}{\pi^{1/2}} \frac{e^{W/kT}E^{1/2}}{h^3} e^{-E/kT}\delta E$$

When this is integrated and made equal to N, it is found that $e^{-W/kT}$ has the value

$$\frac{2(2\pi mkT)^{3/2}}{Nh^3} \quad . \quad . \quad . \quad . \quad (4)$$

and in this case

$$\delta n_E = \frac{2\pi N}{(\pi kT)^{3/2}} E^{1/2} e^{-E/kT}\delta E \quad . \quad . \quad (5)$$

This is the Maxwellian distribution for a gas at temperature T, and is evidently encountered when T is large or when N is small. At low temperatures or high electron density, the electron gas is ' degenerate ', and the distribution is as in Fig. 3, whereas at the other extremes, the distribution is Maxwellian. When N is as high as 10^{22}, $e^{W/kT}$ as given by (4) is of the order 100, even when T is as high as 3,600° K, and the electron gas is therefore fully degenerate. In fact, a value as high as this as given by (4) indicates that it was not true that $E \gg W$, and therefore (4) was not applicable. If equation (4) gives a high value for $e^{W/kT}$, the correct value of W must be obtained from (3).

4. Electrical Conductivity.—It is supposed that the free electrons move randomly in the solid with a mean free path l_0. When an electric field is applied, there is a drift velocity superposed on the random velocity. The free path is terminated by collision with an atom (or ion) of the crystal, and the drift velocity acquired during the previous flight is assumed lost at the collision. Let the

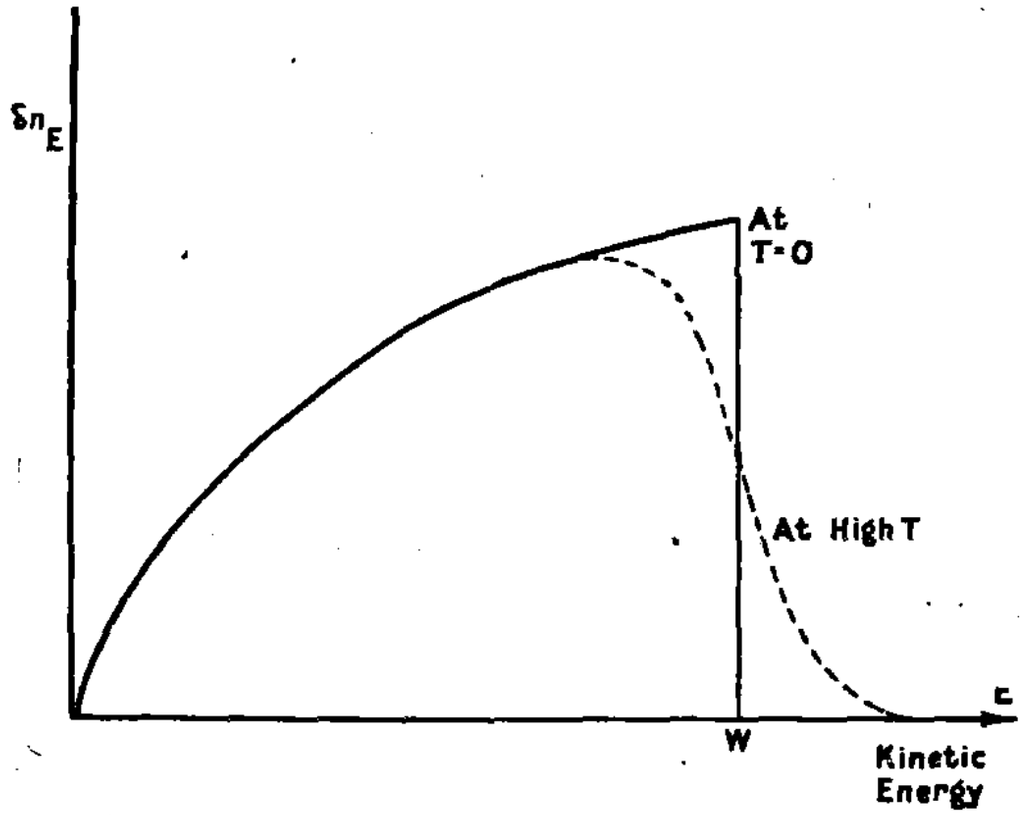

FIG. 3.—Fermi–Dirac energy distribution

applied field be X, then if the charge on the electron is ε, its acceleration in the X direction is $\frac{X\varepsilon}{m}$. If its velocity of random motion is v cm./sec., then the time of flight in the mean free path is $\frac{l_0}{v}$, and the distance drifted in the X direction in this time is $\frac{1}{2}\frac{X\varepsilon}{m}\frac{l_0^2}{v^2}$. Thus the mean velocity of drift is given by $u = \frac{1}{2}\frac{X\varepsilon}{m}\frac{l_0}{v}$ for electrons with velocity v. For all electrons the mean drift velocity becomes:

$$u = \frac{1}{2}\frac{X\varepsilon}{m} l_0 \left(\text{mean value of } \frac{1}{v}\right) \quad . \quad . \quad (6)$$

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If v_m is the maximum speed which an electron can have at zero temperature, the mean value of $\frac{1}{v}$ is easily shown to be $\frac{3}{2v_m}$ for a degenerate electron gas. Then, since

$$W = \tfrac{1}{2}mv_m^2 = \frac{h^2}{2m}\left(\frac{3N}{8\pi}\right)^{2/3},$$

the mean value becomes $\frac{3}{2}\frac{m}{h}\left(\frac{8\pi}{3N}\right)^{1/3}$.

When the drift velocity is u, the current density is $N\varepsilon u$, and the conductivity σ is given by $\sigma = \frac{N\varepsilon u}{X} = N\varepsilon u_0$. u_0, the drift velocity in unit field, is called the 'mobility' of the electron. A more rigid treatment of the mean-drift velocity gives a value 4/3 of that given by (6),[2] thus the present treatment gives finally for σ

$$\sigma = \frac{2\pi\varepsilon^2 l_0}{h}\left(\frac{3N}{8\pi}\right)^{2/3}$$

and the more rigid treatment gives

$$\sigma = \frac{8\pi}{3}\frac{\varepsilon^2 l_0}{h}\left(\frac{3N}{8\pi}\right)^{2/3} \quad . \quad . \quad . \quad . \quad (7)$$

If experimental values of σ are substituted in (7) for a monovalent metal where N is about 10^{22}, it appears that l_0 is several hundred times the interatomic distance. The above theory does not predict this large value, nor does it explain the fact that σ is approximately proportional to $1/T$ (except at low temperatures). It will appear later that the conception of collisions between electrons and atoms is much too crude, and the process is better described as in interaction between the electrons and the thermal vibrations of the lattice. In a perfect lattice at rest, i.e., at zero temperature, there is no interaction and the conductivity should be infinite. The deviations of the lattice from perfection due to impurities and strains produce a residual resistivity ρ_0 at low temperature, and

it is the value of $(\rho-\rho_0)$ which is proportional to temperature. This increase in ρ is due to the increasing movement of the atoms.

Whether the electrons interact directly by collision, or with the thermal vibrations, it is to be noticed that in each case the electrons which take part are confined to those near the top of the Fermi distribution, as in the case of those electrons which are affected by temperature rise. The above theory is accurate only if v is large compared with u, thus in the interactions only a little energy is lost, and since the states of low energy are all occupied, low-energy electrons cannot take part in collisions causing resistance. Similarly, only electrons at the top of the Fermi distribution can be accelerated to contribute to the net flow.

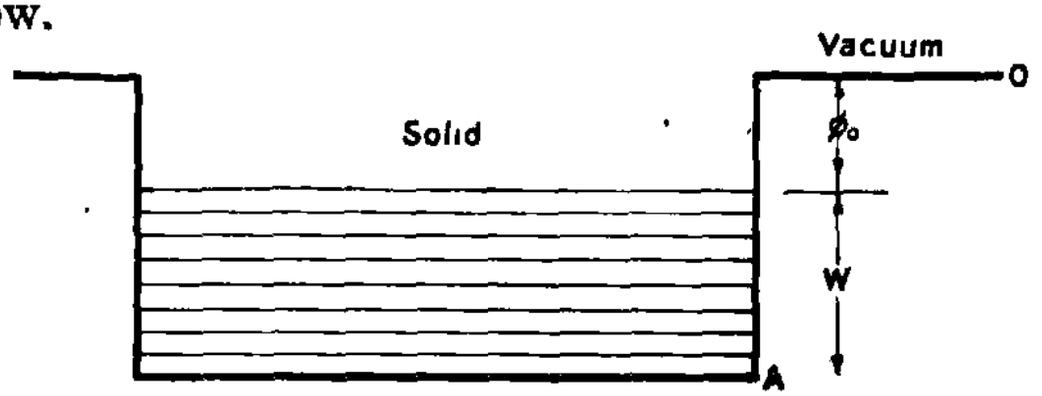

FIG. 4.—Electron levels in a solid at zero temperature

5. Thermionic Emission.—We have seen that at zero temperature, a metal contains electrons with kinetic energy as large as W in Figs. 3 and 4, and that at higher temperatures a fraction of the electrons have greater energy, as in Fig. 3. At low temperatures electrons are not emitted spontaneously from solids, and we therefore know that W in Fig. 4 is less than AO. Clearly, if an electron in the metal at zero temperature can acquire energy ϕ_0 given by AO — W, it may just escape, and will have zero kinetic energy on emergence. The value of AO — W at other temperatures will be described as ϕ, while ϕ_0 is the value of ϕ at absolute zero. ϕ is called the work function of the solid, and is usually measured in electron volts. When the temperature is raised, it is convenient to show in one diagram the energy distribution with the energy scale vertical, and the potential-energy

diagram for a boundary between metal and a vacuum, as in Fig. 5. This involves rotating Fig. 3 to follow the convention of Figs. 1, 2, and 4, i.e., energy increasing upwards. Then the 'tail' in the distribution OP can escape, and those electrons with kinetic energy AP will have energy OP after escape.

While, as stated above, electrons with total energy greater than AO 'may escape', it is clear that if the x direction in a three-dimensional co-ordinate system is made perpendicular to the metal surface, only those

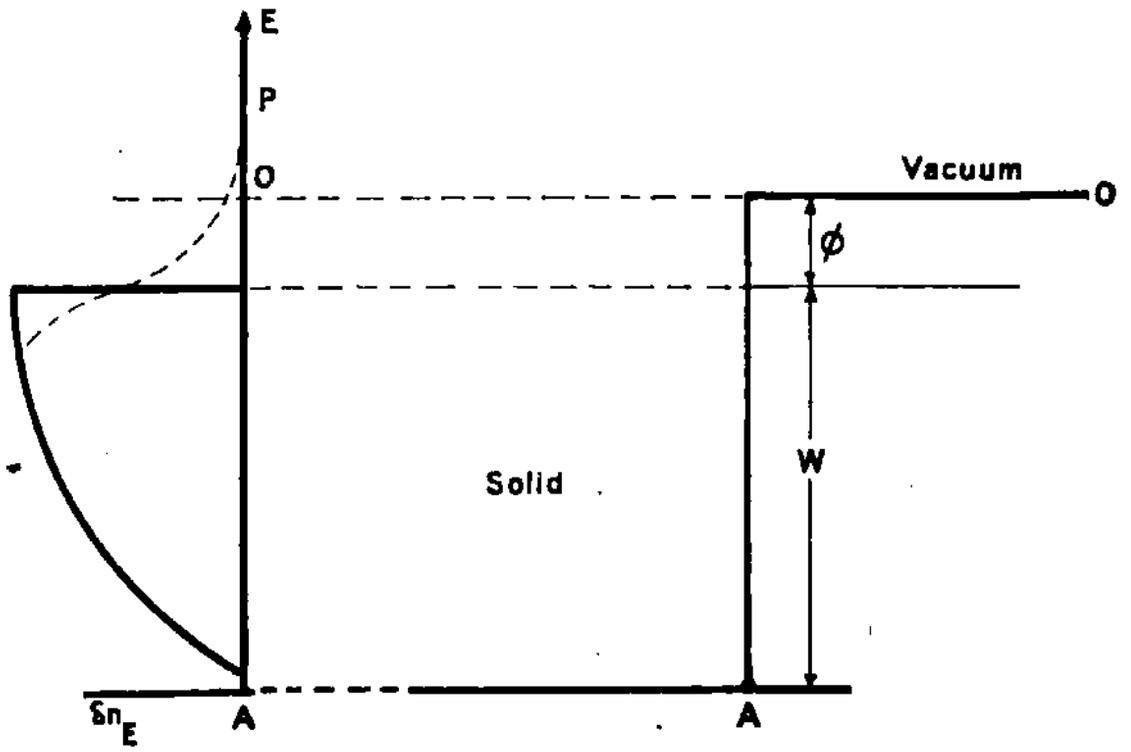

FIG. 5.—Energy distribution in a solid at high temperature

electrons will actually escape whose motion is in the x direction, and whose energy is greater than AO, and then only if there is no surface-reflection effect. We will now calculate the number of electrons which can escape from 1 cm.^{2} of surface at temperature T.

If the total momentum p is the vector sum of p_x, p_y, and p_z, the number of electrons per cm.^{3} with momentum between p and $p + \delta p$ is as in (2)

$$\delta n_p = \frac{8\pi}{h^3} \frac{p^2 dp}{e^{E-W/kT} + 1}$$

Consideration of the volume elements in a co-ordinate system shows that in transforming from polar to rectangular

co-ordinates, the integral over a certain range of a function of p is obtained by replacing the quantity $4\pi p^2 dp$ by the product $dp_x dp_y dp_z$. Similarly, in one plane the product $dp_y dp_z$ replaces $2\pi r dr$, where r is the resultant momentum in the yz plane, i.e., $r^2 = p_y{}^2 + p_z{}^2$. Thus the total number of electrons with momentum between p_x and $p_x + \delta p_x$ is given by

$$\delta n_x = \frac{2\delta p_x}{h^3} \int_0^\infty \frac{2\pi r dr}{e^{\mathrm{E}-\mathrm{W}/k\mathrm{T}} + 1}$$

It is usual to restrict the calculation to the case where, although T is fairly large, E–W is nevertheless large compared with kT, so that unity in the denominator can be neglected.
Since

$$2m\mathrm{E} = r^2 + p_x{}^2,$$

$$\delta n_x = \frac{4\pi}{h^3} \delta p_x \, e^{\mathrm{W}/k\mathrm{T}} \, e^{-p_x{}^2/2mk\mathrm{T}} \int_0^\infty e^{-r^2/2mk\mathrm{T}} \, r dr$$

$$= \frac{4\pi}{h^3} e^{\mathrm{W}/k\mathrm{T}} mk\mathrm{T} \, e^{-p_x{}^2/2mk\mathrm{T}} \, \delta p_x$$

This is the number per cm.^{3} with momentum between p_x and $p_x + \delta p_x$, with values of resultant momentum in the yz plane over the whole range O to infinity.

The total number passing per second through unit area perpendicular to the x direction will be obtained by multiplying δn_x by the velocity v_x, and integrating from O to infinity. However, the number striking unit area of the boundary which can escape is restricted to those with momentum greater than p_a, where $p_a{}^2 = 2m$. OA. Thus the number escaping per unit area becomes

$$n = \frac{4\pi}{h^3} e^{\mathrm{W}/k\mathrm{T}} mk\mathrm{T} \int_{p_a}^\infty e^{-p_x{}^2/2mk\mathrm{T}} \frac{p_x}{m} \delta p_x$$

The current is therefore

$$\mathrm{I} = \frac{4\pi mk\mathrm{T}}{h^3} \epsilon k\mathrm{T} \, e^{\mathrm{W}/k\mathrm{T}} \, e^{-p_a{}^2/2mk\mathrm{T}}$$

$$= \frac{4\pi\epsilon mk^2\mathrm{T}^2}{h^3} e^{-\phi/k\mathrm{T}} = \mathrm{A}_0\mathrm{T}^2 e^{-\phi/k\mathrm{T}}. \quad . \quad (8)$$

The quantity $A_0 = \frac{4\pi\varepsilon mk^2}{h^3}$ has the numerical value $3{\cdot}6 \cdot 10^{11}$ when the current is measured in e.s.u., and 120 when the current is measured in ampères. This, then, is the thermionic-emission formula assuming no surface reflection. It is, of course, necessary to measure the two energies ϕ and kT in the same units. If ϕ is measured in electron volts, k must be measured similarly. It has the value $8{\cdot}62 \times 10^{-5}$ eV. per degree.

6. Photo-electric Emission.—It will be clear from the discussion of Figs. 4 and 5 that a metal at the absolute zero of temperature can just liberate an electron if the electron can acquire energy equal to ϕ_0. The energy associated with light of frequency ν is $h\nu$, and incident light can therefore liberate electrons if its frequency is equal to or greater than ν_0, where in appropriate units

$$h\nu_0 = \phi_0 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The number of electrons liberated will be proportional to the intensity of the light at the required frequency. If the frequency is greater than ν_0, electrons can be liberated with kinetic energy greater than zero, and those which have energy near zero may include electrons from below the top of the Fermi distribution.

At higher temperatures the distribution becomes as in Fig. 5, and the thermionic emission becomes so large that the photo-electric effect is difficult to study. At intermediate temperatures where the thermionic emission is very small, the photo-emission can occur with light of frequency less than ν_0 owing to the 'tail' in the energy distribution above the Fermi level. Thus at room temperature, for example, the threshold frequency ν_0 is not sharply defined.

7. The Work Function.—The theory of free electrons in a metal has given an indication of the value of W, but so far the existence of the work function, i.e., of the fact that W is less than AO, has been deduced from experimental observation, and no theory has been presented which would predict its magnitude. An elementary treatment

can be given in terms of the 'image force', and the surface-polarized layer. When an electron is withdrawn from a metal, the metal is polarized, and the force between the electron and the metal can be represented by the force between the electron and its 'mirror image' in the metal. Thus an electron at a distance x cm. from the surface induces a positive charge ε at x cm. below the surface, provided x is large compared with an interatomic distance and small compared with the area of the surface. There is therefore an 'image' force of attraction $\varepsilon^2/4x^2$. This approach leads to an expression [3] $\varepsilon^2/2r_0$ for the energy to remove an electron from the metal to an infinite distance, where r_0 is of the order of the atomic spacing. This energy is taken to be equal to the work function ϕ, and this treatment indicates that ϕ will be larger for metals of high density.

The potential energy of an electron in the metal referred to zero at infinity is not, however, $-\phi$, but $-(\phi + W)$. The change of magnitude W occurs in passing through the surface electrical field.[3] This is formed because the surface layer of atoms is not in equilibrium under the same forces as atoms in the interior. The change in potential is shown in detail in Fig. 6.

Owing to thermal expansion there are variations with temperature in the interatomic distance, which affects ϕ, in the surface dipole moment, affecting W, and in the electron density N, which also affects W. If ϕ is assumed to increase linearly with T [4], [5] as a result of these changes in ϕ and W,

i.e., $$\phi = \phi_0 + \alpha T$$

then the thermionic emission equation becomes

$$I = \frac{4\pi\varepsilon mk^2}{h^3} T^2 e^{-(\phi_0 + \alpha T)/kT}$$

$$= A_0 T^2 e^{-\alpha/k} e^{-\phi_0/kT} \quad . \quad . \quad . \quad (10)$$

Thus if a 'Richardson' plot is made experimentally of

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