

PHOTOELECTRIC PROPERTIES OF IRON

by

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INTRODUCTION

The phenomena associated with electrons within crystalline solids can be explained by either a classical or a quantum mechanical approach to the electron energy in the solid. Since the latter has given by far the better results (6, 14) for temperatures above absolute zero, it will be used exclusively in the discussion of the work reported in this paper.

The ejection of electrons under the action of electromagnetic radiation is a basic physical process which must be explained in any successful theory of the solid state.

In 1905 and 1906 Einstein (7, 8) made a most important quantum extension to the classical theory by predicting the energy relations between the ejected electron and the incident light to be

$$\frac{1}{2}mv^2 = h\nu - \phi.$$

Here m is the mass of the electron, v is the velocity of the electron, h is Planck's constant, ν is the frequency of the incident light, and ϕ is the minimum energy that must be added to the electron to free it and is called the work function. The energy of the photoelectron is seen to be proportional to the frequency of the incident radiation and independent of temperature, while the number of electrons would seem to be proportional to the light intensity or number of quanta of energy. Also, no electrons are expected to escape when $h\nu < \phi$ or $h\nu < h\nu_0$ where ν_0 is called the threshold frequency.

In order to develop a theory that accounted for a temperature dependence of the photoelectric effect, Sommerfeld in 1928 (16) treated the free electrons as a degenerate gas obeying quantum laws. The potential energy of the electron was assumed to be a constant negative value $-W_a$ inside the metal and zero outside. Thus a potential wall (Fig. 1) was formed which could be surmounted by the electron only if the electron possessed a total energy as great, or greater than, W_a .

It was assumed that the kinetic energy of each electron is quantized to certain discrete levels and that the Pauli exclusion principle is applicable. The latter states that no two electrons can simultaneously occupy the same quantum state. Since a quantum state is specified by the kinetic energy and the spin value, which can be only $\frac{1}{2}$, only two electrons at most could occupy one energy level.

At very low temperatures the electrons are in the degenerate states and tend to occupy the lowest possible energy states. At absolute zero the lower $N/2$ levels are filled when there are N free electrons in the crystal. The highest level filled under these conditions is called u . However, at higher temperatures thermal agitation is great enough to displace some of the electrons previously in energy states near u into levels greater than u . The Fermi-Dirac statistical theory (4, 9) was developed to apply to such a degenerate gas obeying the Pauli exclusion principle. The number of electrons in a given energy level as a function of the temperature and kinetic energy is

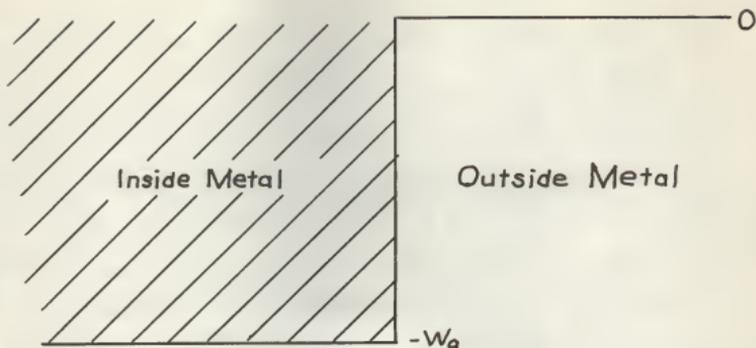


Fig. 1. Potential wall.

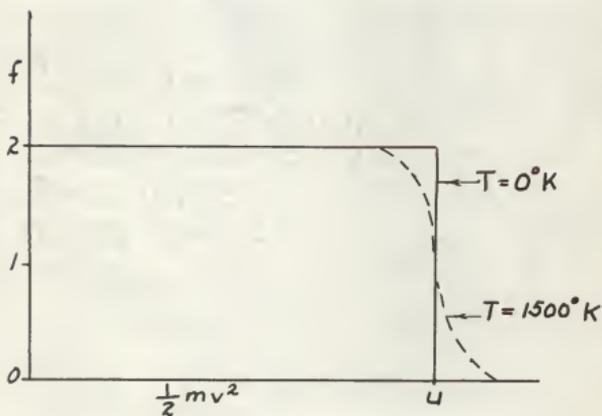


Fig. 2. Distribution of electrons in a given energy level as a function of the temperature and kinetic energy.

$$f = \frac{2}{e} \frac{-(u - \frac{1}{2}mv^2)}{kT} + 1$$

Here f is the number of electrons per energy level, u is the highest energy of an electron at absolute zero, $\frac{1}{2}mv^2$ is the kinetic energy, k is Boltzmann's constant and T is the absolute temperature. A graph of this function is shown in Fig. 2.

The Fermi-Dirac statistics applied to the component of the kinetic energy normal to the metal surface gives a distribution of energies as shown in Fig. 3. It is seen that at sufficiently high temperatures the increased energy due to thermal agitation increases the total energy of some of the electrons to a value equal to, or greater than, W_a . Obviously such electrons will escape from the metal.

Electrons having energy less than W_a can be made to escape if they can be made to absorb a quantum of electromagnetic radiation having sufficient energy to raise the total energy to or above W_a . To account for the liberation of electrons under such conditions, further assumptions are necessary.

The first assumption made is that the electrons are not absolutely free. If they were free, the photon, having a comparatively small momentum, could deliver only a small part of its energy on a single collision. It is also assumed that the entire energy of the absorbed quanta is added to the normal component of the electron's energy. The third assumption, made by Fowler (12), is that the probability of an electron absorbing energy $h\nu$ is approximately independent of the frequency of the radiation and independent of the energy of the electrons for frequencies near the threshold.

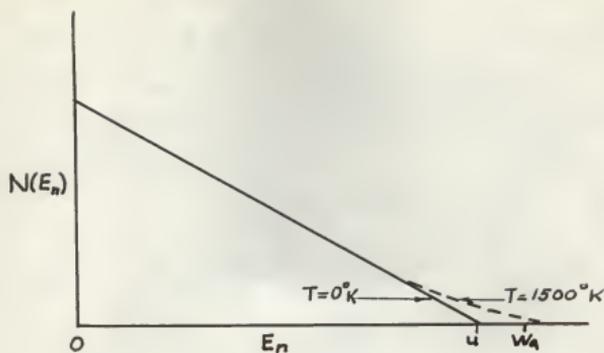


Fig. 3. Distribution of kinetic energies normal to the surface.

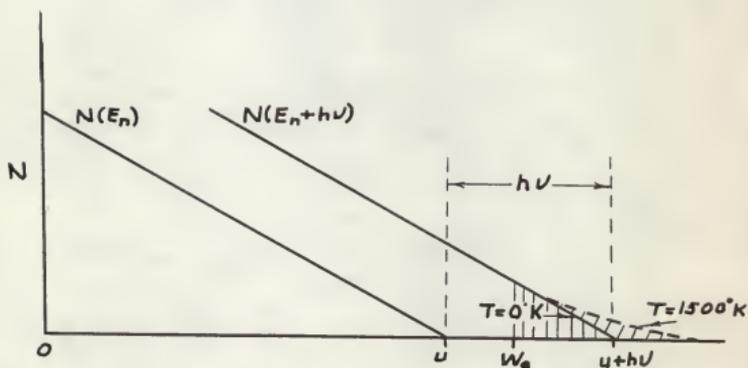


Fig. 4. Shift of normal energy distribution due to electromagnetic radiation.

As a result of these assumptions it can be shown that the absorption of $h\nu$ energy by each free electron will shift the normal energy distribution curve along the axis by an amount $h\nu$ as shown in Fig. 4. This figure thus, in effect, shows that the number of electrons at absolute zero available for ejection is proportional to the area of the shaded triangle formed by the absolute zero curve and $E_n = W_a$. The base is $h(\nu - \nu_0)$ as $W_a - u = h\nu_0$ and the number of escaping electrons is therefore proportional to $(\nu - \nu_0)^2$. At higher temperatures, the number is slightly increased by the area under the tail of the curve. The photoelectric current as a function of frequency is parabolic as shown in Fig. 5. Since $\Delta\nu$ is proportional to $-\Delta\lambda$ for small frequency differences the curves of the photoelectric current as a function of the wavelength are similar as shown in Fig. 6.

Fowler (12) developed a theory that predicts the spectral distribution for frequencies near the cutoff frequency ν_0 . The number of electrons ejected at temperature T is proportional to N_B , the number of free electrons per unit volume within the metal which have a velocity component, v_n , normal to the surface which is greater than v_{n0} , such that

$$\frac{1}{2}mv_{n0}^2 + h\nu = W_a.$$

Application of the Fermi-Dirac statistics dealing with normal energies leads to the relation

$$N_B \sim I = \alpha T^2 (W_a - h\nu)^{-\frac{1}{2}} f(x)$$

or

$$\log \frac{I}{T^2} = B + F(x).$$

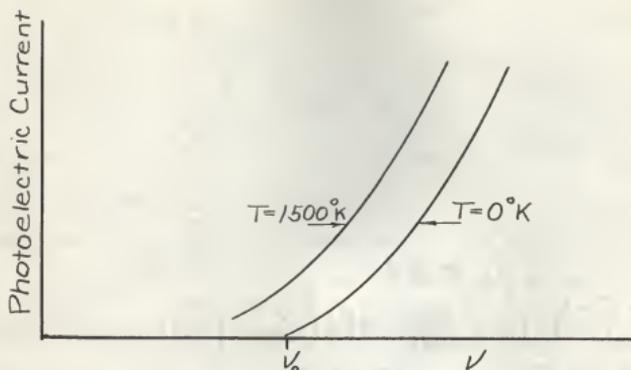


Fig. 5. Theoretical photoelectric current vs. frequency for two temperatures.

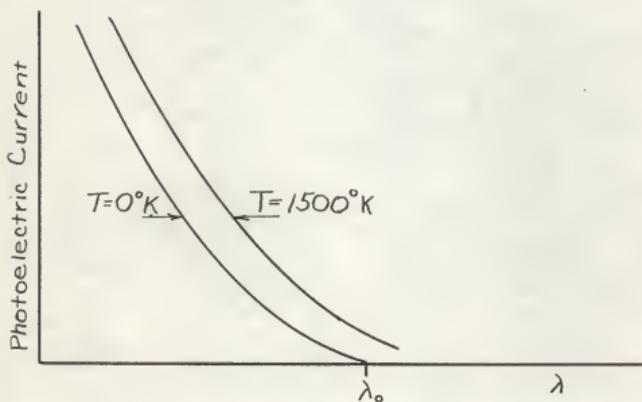


Fig. 6. Theoretical photoelectric current vs. wavelength for two temperatures.

Here the proportionality constant α is a function of the number density of free electrons, $(W_a - h\nu)^{-\frac{1}{2}}$ is nearly constant when the frequency is near the threshold value and $f(x)$ is a universal function of x , whose form is the same for all metals and all temperatures. Also $x = \frac{h(\nu - \nu_0)}{kT}$ and ν_0 is the threshold frequency that would be found in the metal at absolute zero if the same crystal structure and boundary conditions occurred then.

The theoretical curve $F(x)$ may be plotted as a function of x and the observed photoelectric current I plotted in the form $\log \frac{I}{T^2}$ as a function of $\frac{h\nu}{kT}$. These are known as Fowler plots and are shown in Fig. 7.

The horizontal shift required to make the curves coincide is $\frac{h\nu_0}{kT}$, while the vertical shift is B .

B is unimportant in itself in that unknown units of measurement are involved, but the change in B indicates the change in the free electron density. From the above equation it is seen that

$$\log \frac{I}{T^2} = \log \alpha (W_a - h\nu)^{-\frac{1}{2}} + F(x).$$

Thus B is $\log \alpha$ plus a constant since $\log (W_a - h\nu)^{-\frac{1}{2}}$ is considered constant. By letting the proportionality factor α change with temperature by the relation $\alpha_{T^\circ K} = \alpha_{300^\circ K} + \Delta\alpha$, one can determine $\Delta\alpha$ for $T^\circ K$. DuBridge (5) has shown the relationship between α and n , the number density of free electrons to be

$$\alpha = Cn^{-4/3}.$$

The change in free electron density for a temperature T relative to the density at $300^\circ K$ can be calculated by inserting the above

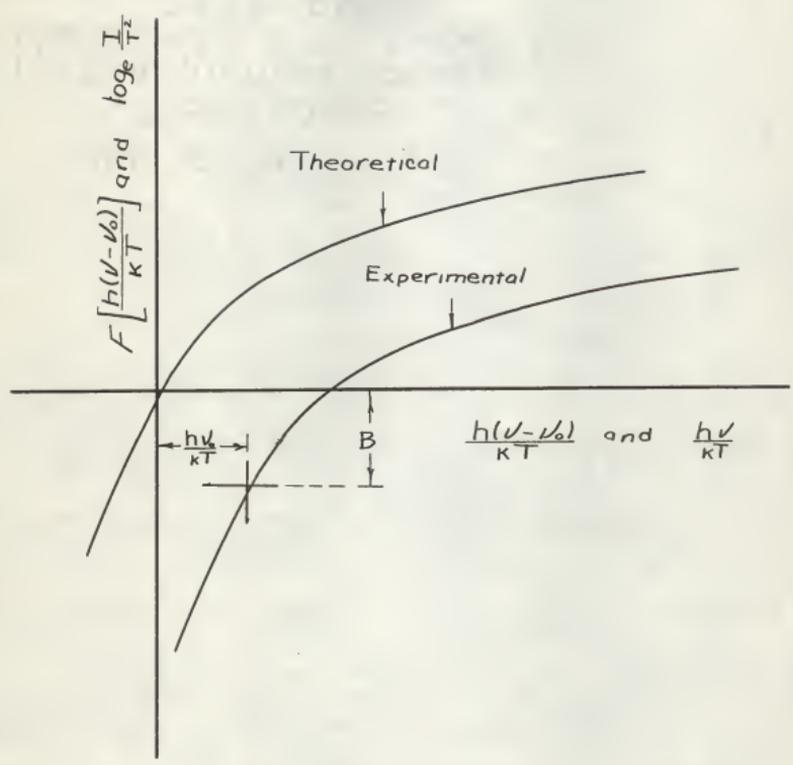


Fig. 7. Theoretical and experimental Fowler plots.

function and its differential in the relationship

$$\Delta B = \log (\alpha + \Delta\alpha) - \log \alpha.$$

This yields $\frac{\Delta n}{n} = \frac{3}{4}(1 - e^{\Delta B})$ and shows that a negative shift corresponds to an increase in free electron density.

The photoelectric properties of a pure metal may be studied accurately only when the surface is as nearly free of contaminations and gas as possible. In order to accomplish this, the sample was subjected to long outgassing processes in a high vacuum system.

Iron was selected for this study as its crystal structure varies with temperature. The correlation of the work function and the number density of free electrons at various points in these states is of interest.

EXPERIMENTAL APPARATUS

The experimental values were determined from an integrated system of apparatus, each part of which is described in detail below.

Experimental Tube

The glass experimental tube contained the spectroscopically pure iron strip suspended by its two ends. The strip, 14 cm long, 4 mm wide, and 0.03 mm thick, was produced by Adam Hilger of London by an electrolytic deposition process.

A molybdenum collecting cylinder surrounded the iron strip to catch the photoelectrons which were repelled from the strip by -135 volts. A quartz window in the glass tube and an opening in the cylinder allowed ultraviolet light to fall upon the strip.

The opposite side of the tube allowed observation of the sample through an optically flat pyrex window and an opening in the collecting cylinder. The collecting cylinder could be rotated by an external magnet in order to protect the windows in the glass envelope from sputtering by the heated iron strip. The tube was enclosed in a metal box for electrostatic shielding.

High Vacuum System

The vacuum system consisted of a three stage oil diffusion pump on one occasion and a mercury vapor pump on another operation backed by a fore pump capable of obtaining a pressure of 10^{-4} mm of mercury. The lowest pressures obtained were of the order of 10^{-8} mm of mercury with the oil diffusion pump and 10^{-7} mm of mercury with the mercury vapor pump. In each case a liquid air trap was used to reduce the pressure and to keep contamination from the pumps out of the experimental tube.

Several weeks pumping was required to reduce the pressure to the above values. The glass system was flamed several times a day and the collecting cylinder was heated inductively to expedite the outgassing process. The sample was heated by a conduction current.

The pressure of the system was determined with a Type VG-1A ionization gauge manufactured by Distillation Products, Inc. A constant electron current through the tube produced a positive ion current proportional to the pressure. Found and Dushman give an excellent description of this type gauge (11).

Radiation Source

Monochromatic light was obtained in the region of 2300 Å to 2650 Å from a mercury arc source and a Bausch and Lomb quartz monochromator. The intensity of the light was measured with an 8 junction bismuth-silver vacuum thermopile placed in the monochromatic beam.

Temperature Measurements

The temperature of the iron sample was determined by observation through a pyrex window in the experimental tube with a Leeds and Northrup optical pyrometer of the disappearing filament type. Temperature corrections for black body emissivity were made from data by Wahlin and Wright (17). The temperatures between red heat and room temperature were interpolated by means of the iron sample heating current.

Electrometer Circuit

The photoelectric current in this research was of the order of 10^{-14} amperes and therefore required a very sensitive current measuring device. A carefully balanced electronic circuit built around a Western Electric 96475 tube with a very high input resistance was utilized. When the photoelectric current input signal was shorted to ground the points contacted by the galvanometer were of equal voltage, but when the signal acted upon the tube an unbalance in the circuit caused the galvanometer to deflect in proportion to the photoelectric current.

The circuit was adjusted for stability as described by Findley (10). Since a difference method was used, an absolute balance with no input was unnecessary.

EXPERIMENTAL RESULTS

The chief interests in this research were the determination of the work function at various temperatures and the associated change in the number density of free electrons.

Data were taken on two samples which were outgassed for approximately 1500 hours at temperatures up to 1300°K .

Figure 8 shows the variation of photoelectric current per unit light intensity as a function of the sample temperature for various wavelengths. These curves give the information necessary to make Fowler plots for any desired temperature in the range from 300°K to approximately 1200°K . Above 1200°K thermionic currents were so great that corrections for them could not be made. The difference method of photoelectric current measurement was used to eliminate small thermionic current readings. This involved measurements with and without the light falling on the iron and hence subtraction of the thermionic currents from the results.

Figure 8 clearly shows definite changes in the slopes of the curves at the Curie temperatures of 1061°K and 1183°K , the temperatures at which crystallographic and magnetic changes occur. Because of these changes Fowler plots were made and analyzed at temperatures both below and above the values at which these changes occur.

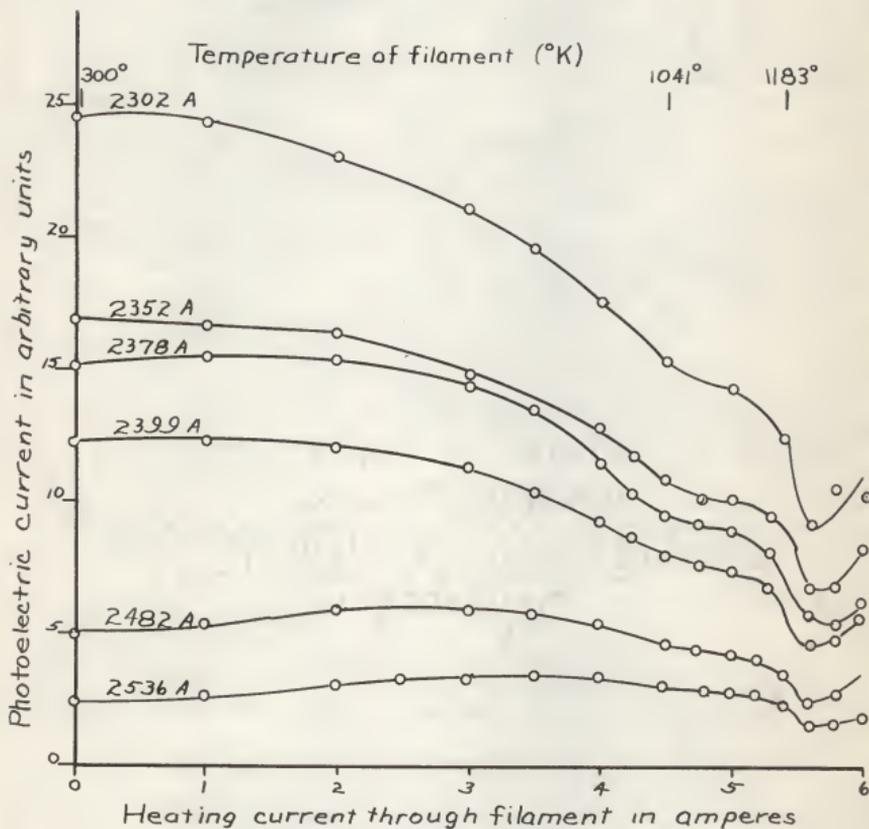


Fig. 8. Photoelectric current per unit light intensity as a function of temperature for various wavelengths.

An example of a Fowler plot obtained from actual data is shown in Fig. 9. The data were obtained at 300°K. The horizontal shift from the theoretical curve, $\frac{h\nu_0}{kT}$, is seen to be 182.4 and the vertical shift, B, is -14.2. The work function is

$$h\nu_0 = kT \times \text{horizontal shift}$$

where the energy is expressed in ergs or

$$\phi = \frac{kT \times \text{horizontal shift}}{1.6 \times 10^{-12}}$$

where the energy is expressed in electron-volts. In the above expressions k is the Boltzman constant, T is the temperature in °K, h is Planck's constant, and ν_0 is the frequency of the threshold radiation. This gives the work function

$$\phi = \frac{1.37 \times 10^{-16} \times 300 \times 182.4}{1.6 \times 10^{-12}} = 4.69 \text{ electron volts.}$$

The two samples produced work functions, vertical shifts, and changes in free electron density for the indicated temperatures and crystal structures as indicated in Table 1. Approximately 35 runs at each temperature were made.

Table 1. Work functions, vertical shifts, and free electron density changes for iron.

Temperature in °K	Crystal structure	Work function in electron-volts	Vertical shift	Percent change of electron density
300	Alpha	4.714 ± 0.007	0.0	0
850	Alpha	4.654 ± 0.008	-0.27 ± 0.035	18
1075	Beta	4.623 ± 0.010	-0.75 ± 0.042	40
1200	Gamma	4.670 ± 0.016	-1.03 ± 0.051	48

Cardwell (1) reported 4.72 electron-volts in 1928 while Glascoe (13) reported 4.71 and 4.77 electron-volts in 1931 for the work function of iron at room temperature.

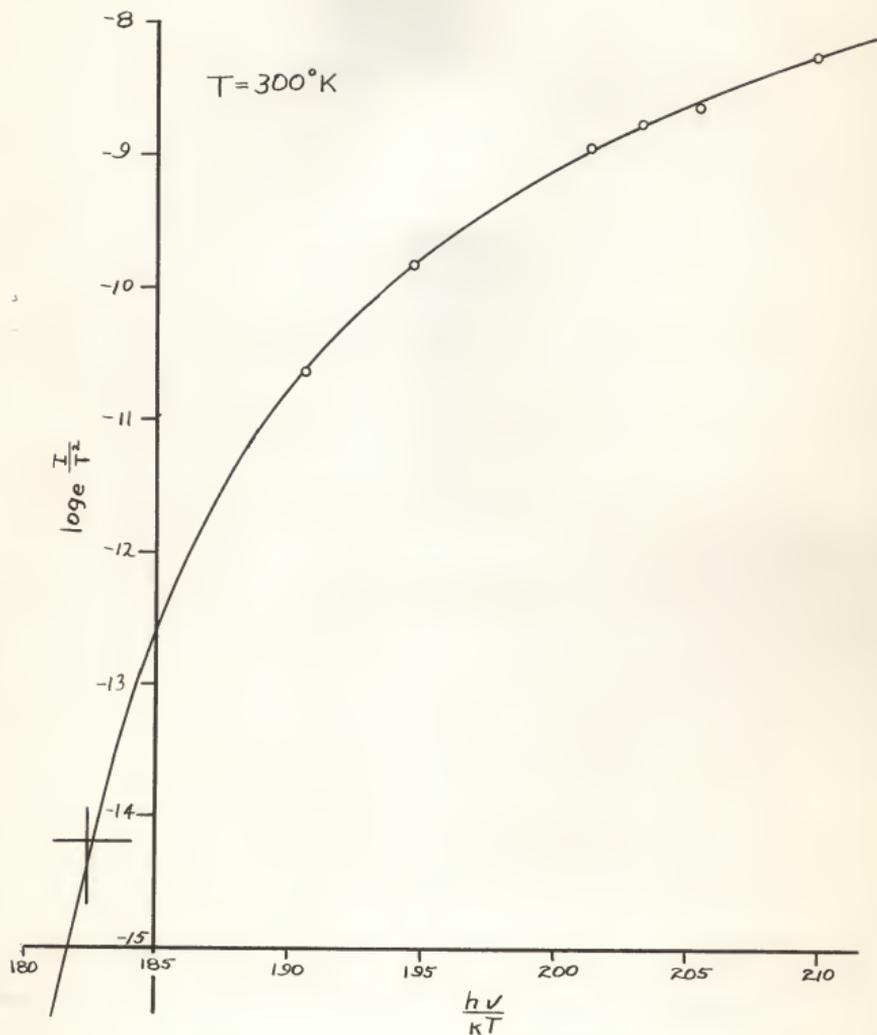


Fig. 9. Experimental Fowler plot for iron at 300°K.

Several results obtained in this work are unexplained by the present theory. These are described below.

The vertical shifts of the experimental Fowler plots relative to the theoretical plot indicates an increase in free electron density with an increase in temperature. The present theory predicts no dependence upon temperature for the free electron density.

A disagreement appears in the photocurrent versus temperature curves shown in Fig. 8. The current decreases as the temperature increases in the α -iron region while theory predicts the current should be nearly directly proportional to the temperature squared.

Figure 10, showing curves of photocurrent versus wavelength, reveals a second disagreement. The upper two curves are plotted for temperatures in the α -iron region and should be more or less parallel instead of crossing as they do. This same crossing of curves has been observed in tantalium by Cardwell (2), in silver by Winch (18), and in gold by Morris (15). It appears to be a real effect which can be explained only by a further expansion of the theory.

CONCLUSIONS

These results are interesting expansions of the work done by Cardwell (3) on nickel, another metal which undergoes a magnetic transformation at low temperatures. It is very obvious that more theoretical work must be done on the theory of the solid state in order to explain the phenomena associated with free electrons in metals which undergo magnetic or crystallographic transformations.

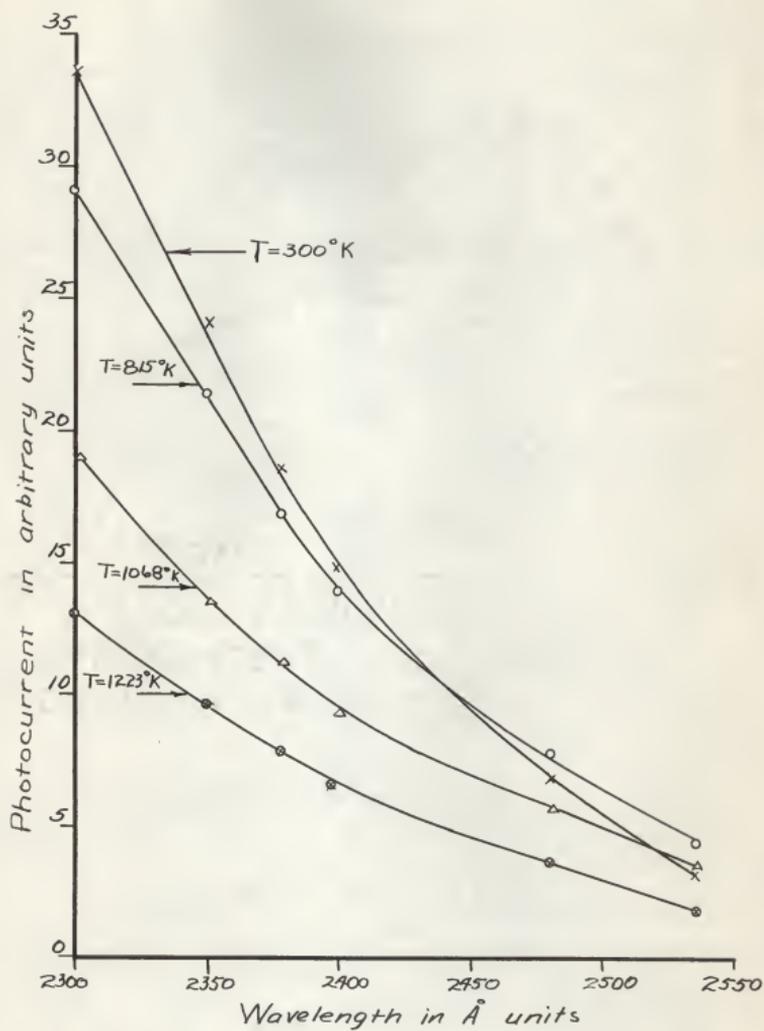


Fig. 10. Photoelectric current as a function of wavelength for various temperatures.

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LITERATURE CITED

- (1) Cardwell, A. B.
The photoelectric and thermionic properties of iron.
Natl. Acad. Sci. Proc. 14: 439-445. June, 1928.
- (2) Cardwell, A. B..
Photoelectric properties of tantalum. Phys. Rev. 38:
2041-2048. Dec., 1931.
- (3) Cardwell, A. B.
Photoelectric and thermionic properties of nickel.
Phys. Rev. 76: 125-127. July, 1949.
- (4) Dirac, P. A. M.
On the theory of quantum mechanics. Proc. Roy. Soc.
112: 661-677. 1926.
- (5) DuBridge, L. A.
New theories of the photoelectric effect. Act. Sci.
et Indust. 268. Paris: Hermann & Cie, 56 p, 1935.
- (6) DuBridge, L. A.
Some aspects of the electron theory of solids.
Amer. Phys. Teach. 7: 357-366. Dec., 1939.
- (7) Einstein, A.
Generation and transformation of light. Ann. der
Phys. 17: 132-148. June, 1905.
- (8) Einstein, A.
Light generation and absorption. Ann. der Phys.
20: 199-206. May, 1906.
- (9) Fermi, E.
Quantization of the ideal monatomic gas. Zeits. f.
Phys. 36: 902-912. 1926.
- (10) Findley, D. E.
Work-function studies on nickel. Unpublished thesis.
Kans. State Col. Agr. and Appl. Sci. 41 p, 1947.
- (11) Found, G. W. and S. Dushman.
Studies with ionization gauge. Construction and method
of calibration. Phys. Rev. 17: 7-19. Jan., 1921.
- (12) Fowler, R. H.
The analysis of photoelectric sensitivity curves for
clean metals at various temperatures. Phys. Rev. 38:
45-56. July, 1931.

- (13) Glascoe, G. N.
Contact potential difference between iron and nickel
and their photoelectric work functions. *Phys. Rev.* 38:
1490-1496. Oct., 1931.
- (14) Hughes, A. L. and L. A. DuBridge.
Photoelectric phenomena. New York: McGraw-Hill, ch 6,
1932.
- (15) Morris, L. W.
Certain photoelectric properties of gold. *Phys. Rev.*
37: 1263-1268. May, 1931.
- (16) Sommerfeld, A.
Electron theory of metals on the basis of Fermi
statistics. *Zeits. f. Phys.* 47: 1-60. Feb., 1928.
- (17) Wahlin, H. B. and R. Wright.
Emissivities and temperature scales of the iron group.
Jour. Appl. Phys. 13: 40-42. Jan., 1942.
- (18) Winch, R. P.
Photoelectric properties of silver. *Phys. Rev.* 37:
1269-1275. May, 1931.

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The quantum mechanical theory of photoelectric emission from a crystalline material is reviewed. In this development the Fermi-Dirac statistical theory applying to a degenerate gas obeying the Pauli exclusion principle is used in order to find the distribution of kinetic energies normal to the surface. As long as the normal kinetic energy is less than the potential wall W_a formed by the bonds between the electron and the nucleus, the electron cannot escape.

A photoelectron can be produced by augmenting the normal kinetic energy with electromagnetic radiation provided the sum of these two are equal to or are greater than W_a .

The development of this theory leads to the prediction that the shape of curves of photocurrent versus frequency and photocurrent versus wavelength is parabolic.

The Fowler method of analysis is summarized. This method compares experimental curves with a theoretical curve to yield the work function and number density of free electrons.

A description is given in some detail of the experimental apparatus consisting of the experimental tube, vacuum system, radiation source, temperature measuring device and electrometer circuit.

The Fowler method of analysis was applied to data on iron. The work function was found to be 4.714 ± 0.007 electron-volts at 300°K and slightly lower at higher temperatures. The free electron density increased with an increase in temperature; the increase in density at 1200°K over that at 300°K was found to be nearly 50 percent.

The present theory is very inadequate for analysis of materials undergoing crystallographic and/or magnetic changes. Three results are unexplainable by the present simplified theory. First, the free electron density has no temperature dependence in theory. Next, the experimental plots of photocurrent versus wavelength for two temperatures in the same crystal range definitely cross while the theoretical curves are parallel. Last, a disagreement appears in the photocurrent versus temperature curves. The current decreases as the temperature increases in the α -iron region while the present theory predicts the current should be nearly directly proportional to the temperature squared.