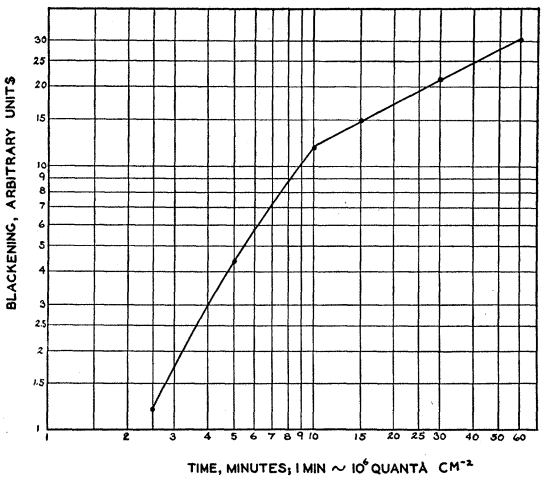

FIG. 3. Blackening of film exposed to x-rays.

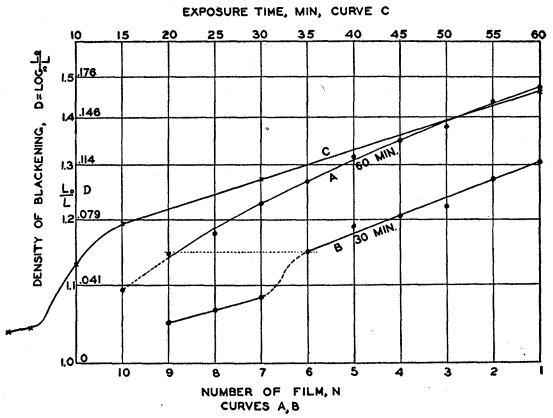

FIG. 4. Blackening of films through which the x-ray beam passed successively.

In another series of exposures, the beam of x-rays passed successively through 10 thicknesses of film, in the manner used by Brindley and Spiers.[12] The blackening of successive films was then measured with a densitometer. Curves *A* and *B*, Fig. 4, show the results for exposures of 60 and 30 minutes. The densities of blackening shown on these curves are very much smaller than those given by Brindley and Spiers; the two sets of data may accordingly be regarded as complementary, within the limits of the equivalence of the wave-lengths of the incident x-rays and the unknown equivalence of characteristics of the films used.

The authors wish to express their appreciation to Dr. W. F. G. Swann for his discussions of the problem and his interest in the investigation.

[12] G. W. Brindley and F. W. Spiers, Phil. Mag. **16**, 686 (1933).

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A Contribution to the Theory of Barrier Layer Cells

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It is shown that the theory of the photovoltaic effect developed by Frenkel and Joffe is incomplete because it contains no adequate explanation of the direction of flow of the current. The proper direction of current flow follows as a natural consequence if the great difference in rate of energy loss by photoelectrons in the semiconductor and the metal is taken into account. In the metal collisions between photoelectrons and conduction electrons are frequent, and transfer of energy is rapid, whereas in the semiconductor such collisions are infrequent, and transfer of energy by elastic collisions of a photoelectron with atoms is slow. Hence rapidly moving photoelectrons tend to migrate into the metal and there lose their energy and become trapped.

INTRODUCTION

A BARRIER layer photo-cell such as the Cu_2O or Se cell consists of a closed conducting circuit which comprises a semiconductor forming a link in a metallic circuit, and a very thin barrier to the passage of electrons between the metal and semiconductor at one junction. In order for the cell to function, ionization must be produced in the semiconductor close to the barrier layer. This causes a continuous flow of electrons across the barrier layer from the semi-

conductor to the metal, around the metallic part of the circuit and back to the semiconductor.

Conditions the Theory Must Satisfy

To account for such an effect, it must be shown not only that the action of light causes electrons in the semiconductor to cross the barrier into the metal, but that after conditions of steady flow have been established, these electrons do not return to the semiconductor across the same barrier. Expressing these conditions algebraically:

$$N_1 > N_3, \tag{1}$$

where N_1 = number of electrons crossing the barrier from semiconductor to conductor; N_2 = number of electrons crossing the other boundary from semiconductor to conductor; N_3 = number of electrons crossing the barrier from conductor to semiconductor and N_4 = number of electrons crossing the other boundary from conductor to semiconductor.

After a steady current flow has been established, there must be no net gain or loss of electrons by the semiconductor. Hence

$$N_1 + N_2 = N_3 + N_4. \tag{2}$$

Therefore if N_1/N_3 is increased by the action of light, N_2/N_4 is decreased, and

$$N_1/N_3 > N_2/N_4. \tag{3}$$

The necessary conditions for a steady current having now been formulated, it remains to establish a mechanism which will meet these conditions.

Discussion of the Theory of Frenkel and Joffe

Frenkel and Joffe[1] have published a theory of the photovoltaic effect utilizing the same concept which they employed so effectively to explain the Cu_2O rectifier. This theory seems incomplete in certain respects, but by introduction of a neglected factor it may be made adequate to explain the facts.

In their treatment there is a marked difference in the potential energy levels of the conduction electrons in the metal and in the semiconductor, the conduction levels in the semiconductor being at a higher potential. Equilibrium between the two is established when the transfer of electrons across the barrier is the same in both directions.

The photovoltaic effect is assumed to result from ionization of the semiconductor near the barrier layer, and transfer of photoelectrons across the barrier into the metal. In order to explain the fact that a higher quantum energy is required to produce the photovoltaic effect than is required to produce photoconduction, they show by wave mechanics that the probability of transmission through the barrier layer increases with increasing kinetic energy. Hence the barrier is a smaller obstacle to photoelectrons of high kinetic energy than to those of low kinetic energy, and photoelectrons of high kinetic energy will therefore dominate in the resultant photocurrent.

The deficiency of the theory of Frenkel and Joffe lies in the fact that no good reason is given for the direction of electron flow. In fact, one would expect the flow to be opposite to that found by experiment, because of the following considerations. First, the energy to extract an electron from a bound state in the semiconductor, and give it sufficient energy to penetrate the barrier, is certainly as high as and probably somewhat higher than the energy necessary to extract an electron from the metal and give it the same kinetic energy with which to penetrate the barrier. Second, the optical absorption coefficient of the metal is much higher than that of the semiconductor, and one would therefore expect a greater concentration of photoelectrons close to the barrier in the metal, than in the semiconductor. One would therefore expect more electrons to enter the semiconductor than to enter the metal.

The contribution to the steady current of electrons which have lost their photoelectric velocities is zero. This conclusion may be reached either from theoretical or experimental considerations. It has previously been mentioned that more energetic quanta are required to produce the photovoltaic effect than to produce photoconduction, from which we can conclude that slow photoelectrons do not enter into the

[1] J. Frenkel and A. Joffe, Phys. Zeits. d. Sow. **1**, 1 (1932).

photovoltaic effect. When a steady state has been reached in the dark there are as many electrons entering as leaving the semiconductor. Under these conditions the probability of a thermally freed electron leaving the semiconductor by a particular route must be equal to the probability of its replacement by an electron entering by the same route. If it were otherwise a continuous current could flow under conditions of thermodynamic equilibrium. Since an electron which has lost its photoelectric velocity is indistinguishable from one thermally freed, it cannot contribute to the photovoltaic current.

Modified Theory

The theory becomes adequate if the great difference in the rate of loss of velocity of a photoelectron in the semiconductor and the metal is taken into account.

According to present views, the concentration of free electrons in semiconductors is very much lower than it is in conductors, and therefore collisions between free electrons in the semiconductor are very rare. The photoelectrons, unless they have enough energy to excite electrons in bound states will have to lose their kinetic energy by collisions with whole atoms. Because of the great difference in mass between electrons and atoms, electrons will lose their energy very slowly. In fact, if we assume the space lattice of Cu_2O to be composed of free elastic spheres having the masses of Cu and O atoms, an electron will still possess about half its initial kinetic energy after 15,000 collisions. This figure is given for order of magnitude only. Because of this slow energy loss an electron is able to migrate distances many free paths in length through the semiconductor before it loses its photoelectric energy, and may collide with the barrier layer many times before its energy is lost; hence both the chance of an electron crossing the barrier and the volume of the semiconductor effective in supplying electrons is increased by the slow loss of energy.

Under equilibrium conditions equipartition of energy between atoms and electrons necessarily holds, but the deviation of electron velocities from the mean in the semiconductor is much less than that of the atoms, or of the electrons in the metal, because the individual gains and losses of energy by collision are a much smaller proportion of the total energy of the electrons. At first sight this might appear to violate the equilibrium requirement that the number of electrons crossing the barrier must be the same in both directions for electrons of all energies. But while high velocity electrons are much more numerous in the metal, their chance of entering the semiconductor, and staying long enough to gain equilibrium with it is small, because of the great number of collisions required and the high probability of return across the barrier before the energy loss has been achieved. It is therefore obvious that a photoelectron possessing considerably more than the mean thermal energy will have a relatively high probability of crossing the barrier and quickly losing its excess energy in the dense electron atmosphere of the metal, whereas a similar photoelectron originating in the metal will have a very low probability of accomplishing the reverse process. Hence $N_1/N_3>1$ in the presence of light and by Eq. (2) $N_1/N_3 > N_2/N_4$.

The time during which a photoelectron will maintain a high kinetic energy in the conductor is very short as it can rapidly lose its energy in the dense electron atmosphere because the energy of a photoelectron is above the top of the fermi distribution. Therefore photoelectrons entering the metal from the semiconductor will have a low probability of return, whereas the photoelectrons which escape from the metal into the semiconductor have a very high probability of return. Therefore N_1 is markedly increased by the presence of photoelectrons whereas N_3 is not. From Eq. (2) it follows that an increase in N_1/N_2 results in a decrease in N_3/N_4 therefore expression (3) holds, and a current will flow.

Experimental Support of the Modified Theory

This theory accounts easily for the results obtained by Schottky[2] which lead him to surmise that photoelectrons freed in the semiconductor are able to make a great many collisions and still succeed in crossing the barrier layer. It will

[2] W. Schottky, Phys. Zeits. **32**, 833 (1931).

also explain the failure of Nasledow and Nemenow[3] to produce a barrier layer cell in which electrons would flow from the metal to the semiconductor, for even though a copious emission of electrons were obtained from the metal, most of the electrons would return to the metal before they lost their kinetic energy.

The author wishes to thank Dr. Felix Bloch and Dr. Robert Oppenheimer for valuable help and criticism.

[3] D. N. Nasledow and L. M. Nemenow, Phys. Zeits. d. Sow. 3, 1 (1933).

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Sparking Potentials at Low Pressures

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Sparking potentials were observed between outgassed nickel electrodes in air at low pressures. The spark length d was varied from 2–10 mm and the pressure p reduced from 1 mm of mercury to 0.06 mm. Sparking potentials as high as 80,000 volts were observed, and agreed approximately with Paschen's law. The sparking potential V for $p \cdot d < 0.95$ is given by $p \cdot d \cdot e^{V/136,500} = 1$.

IT is well known that as the pressure of a gas diminishes, the potential difference necessary to produce a spark discharge between flat electrodes, separated by a fixed distance, also diminishes, until at a critical pressure the sparking potential reaches a minimum value. Below this critical pressure the potential required to produce a discharge, rapidly increases as the pressure is lowered.

Many experiments were made by Peace,[1] Paschen[2] and Carr[3] to check Paschen's law, which stated that at a given potential difference, the field being uniform, the product of the pressure at which the discharge occurs and the distance between the electrodes is constant. This law seems to be fairly established experimentally thus far.

Carr[3] who carried the investigation below the critical pressure found that the sparking potential rose extremely fast as the pressure was lowered but he was only able to reach a voltage of 1800 volts due to the restrictions in the design of his apparatus. The portion of the curve beyond this voltage has not as yet been investigated. Many experiments involve the use of electrodes close together, with gas pressures and potentials bordering on those at which a spark takes place; thus it is of interest to know just when such a discharge may occur. This investigation was carried out with this point in view. The experiments described in this paper deal with sparking potentials in air with nickel electrodes. Carr[4] has shown that the sparking potentials of almost all the common gases with the exception of hydrogen are grouped very closely around that of air in the low range of pressures.

APPARATUS

A high voltage transformer and a kenotron supplied the rectified high voltage. A microammeter in series with Shallcross high resistances and a Kelvin electrostatic voltmeter served as a means of measuring the potential difference across the discharge tube, that is, between the electrodes. Since no condenser was used in the rectified high voltage, the microammeter resistance method with half wave rectification gave average values of the voltages read, which were multiplied by π in order to give the peak voltages that were interpreted as the sparking potentials.

[1] L. R. Peace, Roy. Soc. Proc. **A62**, 111 (1889).
[2] E. T. Paschen, Ann. d. Physik **37**, 69 (1889).
[3] W. R. Carr, Phil. Trans. Roy. Soc. **201**, 403 (1903).
[4] W. R. Carr, Phil. Trans. **A201**, 410 (1903).