

## Theory of Rectification of an Insulating Layer

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(Received July 9, 1948)

The problem treated is the rectification by a blocking layer of low inherent conductivity. The potential distribution is determined by the space charge due to free, current-carrying charge instead of by that due to fixed charge. The difference between this case and that treated by previous theories is pointed out. The theory is applied to copper oxide rectifiers. The result is found to agree with experimental results better than the previous theories. The applicability of the theory to other cases is also discussed.

### INTRODUCTION

RECTIFICATION at the contact between different solids depends upon the existence of a blocking layer, which may be classified into two types: natural and artificial blocking layers. A natural blocking layer is one that is produced as the result of the contact. A metal and a semiconductor brought into contact may give rise to such a blocking layer in the semiconductor even when the semiconductor is homogeneous to begin with. If one of the two materials in contact has inherently a layer of different properties or if a thin layer of entirely different material exists at the boundary, then we may have an artificial blocking layer.

A conducting material in its normal state has a certain density of free charge (electrons or holes) which is balanced by an equal density of fixed charge of opposite sign. If the layer of substance playing the role of the blocking layer has a conductivity lower than its normal conductivity, then it must have a lower than normal density of free charge. This is true for all natural blocking layers. For efficient rectification the density of free charge in the blocking layer must be greatly reduced below its normal value and, therefore, becomes negligible in comparison with the density of fixed charge. The potential distribution in the blocking layer is determined by fixed space charge. We have then a simple problem of electrostatics. Most rectifier theories deal with such cases.

In the case of artificial blocking layers the density of free charge need not be lower than its normal value. If the layer is inherently a good

insulator, it may acquire a much higher than normal density of free charge when it is put in contact with two conducting materials. Mott<sup>1</sup> is first to treat artificial blocking layers. He assumes a straight line potential distribution neglecting space charge due to both free and fixed charges. Such an assumption cannot be a good approximation over a wide range of current. The theory of artificial blocking layers is of practical interest. A number of practical problems involve such layers. Copper oxide rectifiers are known to have near the contact a layer of much lower conductivity than that of the bulk of the oxide.<sup>1,2</sup> Certain oxide cathodes have been shown to possess a layer which is of different composition, has much lower conductivity, and shows rectification.<sup>3</sup> De Boer and van Geel<sup>4</sup> and Hartmann<sup>5</sup> have shown that a layer of good insulator (e.g., shellack, mica, sulfur) put between two conducting materials gives rise to rectification. It cannot be readily decided whether blocking layers in all these cases have higher than normal density of free charge throughout the range of operation. It is certain, however, that all artificial blocking layers have excess free charge density for large currents in the direction of easy flow. It is our purpose to treat the problem of blocking layers with excess density of free charge where the influence of the fixed charge on the potential distribution is negligible in comparison. It is immaterial for the

<sup>1</sup> N. F. Mott, Proc. Roy. Soc. **A171**, 27 (1939).

<sup>2</sup> W. Schottky and E. Spenke, Wiss. Veroff. Siemens-Werke **18**, 225 (1939).

<sup>3</sup> A. Eisenstein, Phys. Rev. **71**, 473 (1947); W. E. Mutter, Phys. Rev. **72**, 531 (1947).

<sup>4</sup> J. H. de Boer and W. Ch. van Geel, Physica **2**, 309 and 321 (1935).

<sup>5</sup> W. Hartmann, Physik. Zeits. **37**, 862 (1936).

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treatment whether we have conduction by electrons or by holes. To be definite we shall assume conduction by electrons.

### THEORY

Under equilibrium condition the blocking layer has a definite density of free electrons at each boundary determined approximately by the difference between the inner potential  $\mathfrak{x}$  (energy of the bottom of the conduction band) of the layer and the work function of the material in contact at that boundary  $\phi$ . When the work functions of the two materials in contact with the layer are different, the layer will have different densities of free electrons at the two boundaries. With a fraction of one ev's difference between the work functions the ratio of the electron densities  $n_1/n_2 = \exp[(\phi_2 - \phi_1)/kT]$  becomes very large. It is usually assumed that the blocking layer has a constant density of free electrons at each boundary independent of the current if the material in contact is a good conductor. Actually we have the bottom of the conduction band at the boundary of the blocking layer at a constant level  $(\phi - \mathfrak{x})$  above the Fermi level of the conductor. This is because when two materials of different conductivities are in contact there is comparatively little potential variation in the better conducting material caused by the contact.<sup>6</sup> With constant  $(\phi - \mathfrak{x})$  the boundary density of electrons will not, however, be constant with changing current. In equilibrium the electron current crossing the boundary in either direction is the same and equal to<sup>7</sup>

$$en_0(kT/2\pi m)^{\frac{1}{2}},$$

where  $n_0$  is the boundary density of electrons in the blocking layer when  $i=0$ . When a net current of electrons  $i$  is crossing the boundary into the blocking layer, the electron current crossing the boundary from the blocking layer is

$$en_i(kT/2\pi m)^{\frac{1}{2}},$$

where  $n_i$  is the boundary density of electrons at current  $i$ . With constant  $(\phi - \mathfrak{x})$  the electron current coming from the other side is the same as

in equilibrium. Therefore

$$\begin{aligned} i &= en_0(kT/2\pi m)^{\frac{1}{2}} - en_i(kT/2\pi m)^{\frac{1}{2}}, \\ n_i &= n_0 - (i/e)(2\pi m/kT)^{\frac{1}{2}}. \end{aligned}$$

Consequently our boundary conditions are<sup>8</sup>

$$\begin{aligned} n_1 &= n_{10} - (i_{12}/e)(2\pi m/kT)^{\frac{1}{2}}, \\ n_2 &= n_{20} + (i_{12}/e)(2\pi m/kT)^{\frac{1}{2}}. \end{aligned} \quad (1)$$

For large  $i$ ,  $n_1$  reduces to zero and we have saturated emission from the conductor 1. For a given system we are given  $n_{10}$ ,  $n_{20}$  and the thickness of the layer  $L$ . We can easily calculate  $n_1$  and  $n_2$  for each value of the current. Our problem then is to determine the potential drop across the blocking layer for given  $n_1$ ,  $n_2$ ,  $L$ , and  $i$ .

The Poisson equation is

$$dE/dx = (4\pi e/\kappa)n,$$

where  $\kappa$  is the dielectric constant of the blocking layer. We shall assume that the motion of electrons can be determined in terms of diffusion coefficient  $D$  and mobility  $b$ . In the case of natural blocking layers, sometimes the layer is so thin that it is comparable with the electron mean free path or the electric field is so high that the energy gained per mean free path is higher than the average energy exchange per collision.<sup>9</sup> For such cases diffusion coefficient and mobility lose their meanings. For artificial blocking layers we are not likely to have such troubles. The current is then given by

$$i = nebE - eD(dn/dx).$$

We shall take  $i$  to be the electron current and  $E$  the force on unit negative charge. Then  $e$  and  $b$  are positive and the potential is given by  $V = \int Edx$ . Schottky and Spence<sup>2</sup> have shown that these equations can be simplified by expressing the factors involved in a system of rational units:

$$\begin{aligned} p &= n/N, \quad \gamma = i/i_0, \quad \epsilon = E/E_0, \\ v &= V/V_0, \quad \xi = x/x_0, \end{aligned} \quad (2)$$

where the unit of density of electrons  $N$  is arbitrary.

<sup>8</sup> After these results had been derived the author came upon the work of R. G. Sachs, NDRC Div. 14 Report 129 (1942) who arrived at the same results by a more elaborate analysis.

<sup>9</sup> H. A. Bethe, RL Report No. 43-12 (Nov. 23, 1942).

<sup>6</sup> H. Y. Fan, Phys. Rev. **62**, 388 (1942).

<sup>7</sup> R. H. Fowler, *Statistical Mechanics* (1936), p. 347.

trary and the other units are

$$\begin{aligned} i_0 &= 2ebN^{\frac{1}{2}}(\pi kT/\kappa)^{\frac{1}{2}}, \\ E_0 &= 2N^{\frac{1}{2}}(\pi kT/\kappa)^{\frac{1}{2}}, \\ V_0 &= kT/e, \\ x_0 &= (1/2e)N^{-\frac{1}{2}}(\kappa kT/\pi)^{\frac{1}{2}}. \end{aligned} \quad (3)$$

All the units depend upon the unit of density  $N$  chosen, except the unit of potential which depends upon the temperature only. We shall take  $N$  to be the smaller of the two boundary values  $n_1$  and take the origin  $x=0$  to be at this boundary. With the relation  $b/D=e/kT$  the Poisson equation for current reduce to:

$$\begin{aligned} d\epsilon/d\xi &= p, \\ \epsilon p - (dp/d\xi) &= \gamma. \end{aligned} \quad (4)$$

The boundary conditions are  $p=1$  at  $\xi=0$  and  $p=p_2=n_2/n_1$  at  $\xi=L/x_0=l$ . Integrating we get

$$(d\epsilon/d\xi) - (\epsilon^2/2) + \gamma\xi + \text{const.} = 0, \quad (5)$$

or

$$(d\epsilon/d\xi) - (\epsilon^2/2) + \gamma(\xi+C) = 0. \quad (6)$$

Let  $\zeta = \xi + C$  and

$$u = \exp\left[-\frac{1}{2}\int \epsilon d\zeta\right] = \exp\left[-\frac{1}{2}\int \epsilon d\xi\right] = \exp(-\frac{1}{2}v).$$

We get

$$d^2u/d\zeta^2 = \frac{1}{2}\gamma\zeta u.$$

For  $\gamma > 0$ , i.e., for electron current from the boundary of low electron density,  $p=1$ , to the boundary of high electron density,  $p=p_2$ , we get

$$d^2u/d\theta^2 = \theta u, \quad (7)$$

where

$$\theta = \zeta[\gamma/2]^{\frac{1}{2}} = (\xi+C)[\gamma/2]^{\frac{1}{2}}. \quad (8)$$

For  $\gamma < 0$  it is more convenient to treat it as a current  $\gamma' > 0$  flowing from a boundary  $p_1' = 1$  at  $\xi' = 0$  to the boundary  $p_2' = n_1/n_2$  at  $\xi' = l'$ . The quantities are now rationalized with  $N = n_2$ . Equation (7) is known as Stokes equation. When the quantities involved are all real, it is convenient to express the solution in terms of Airy integrals:

$$u = AAi(\theta) + BBi(\theta). \quad (9)$$

The values of  $Ai(\theta)$  and  $Bi(\theta)$  can be found elsewhere in tables.<sup>10</sup> The potential is given by

$$-\frac{1}{2}v = \ln A + \ln[Ai(\theta) + (B/A)Bi(\theta)]. \quad (10)$$

Putting  $v=0$  at  $\xi=0$  we have

$$-\frac{1}{2}v = \ln[Ai(\theta) + (B/A)Bi(\theta)] - \ln[Ai(\theta_0) + (B/A)Bi(\theta_0)]. \quad (11)$$

The constants of integration  $B/A$  and  $C$  involved in  $\theta$  and  $\theta_0$  are to be determined by the boundary values of  $p$ . The field intensity is

$$\begin{aligned} \epsilon &= dv/d\xi = dv/d\zeta = -(2/u)(du/d\zeta) \\ &= -2(\gamma/2)^{\frac{1}{2}}[Ai'(\theta) + (B/A)Bi'(\theta)] / [Ai(\theta) + (B/A)Bi(\theta)]. \end{aligned} \quad (12)$$

Equation (6) gives

$$p = (\epsilon^2/2) - \gamma(\xi+C). \quad (13)$$

So the boundary conditions are

$$\begin{aligned} p_1 = 1 &= [\epsilon^2(\theta_0)/2] - \gamma C, \\ p_2 = n_2/n_1 &= [\epsilon^2(\theta_2)/2] - \gamma(l+C). \end{aligned} \quad (14)$$

The determination of the integration constants would involve laborious calculation. Fortunately, the properties of the functions  $Ai(\theta)$  and  $Bi(\theta)$  are such that for large values of  $v$  a great simplification results. Since the unit of  $v$ ,  $kT/e$ , is very small, we shall be interested primarily in large values of  $v$ . The details of the method of calculation are given in the appendix.

The solution (7) is inapplicable for  $\gamma=0$  because then we cannot go from (5) to (6). Equation (5) can in this case be written

$$d\epsilon/d\xi = (\epsilon^2/2) + (\kappa^2/2). \quad (15)$$

The solution is obtained by straightforward integration:

$$\begin{aligned} \epsilon &= \kappa \tan(\kappa/2)(\xi + \kappa_1), \\ p &= \kappa^2/2 \cos^2(\kappa/2)(\xi + \kappa_1). \end{aligned} \quad (16)$$

The integration constants are determined by boundary values of  $p$ :

$$\begin{aligned} \cos^2(\kappa\kappa_1/2) &= \kappa^2/2, \\ \cos^2(\kappa/2)(l + \kappa_1) &= \kappa^2/2p_2. \end{aligned} \quad (17)$$

For comparison with experimental results, the slope of  $v$  versus  $\gamma$  curve at  $\gamma=0$  is often important. This resistance can be calculated in the following manner. From the second of the general equations (4) we get, upon integration,

$$v = \gamma \int_0^l (d\xi/p) + \ln(p_2/p_1).$$

<sup>10</sup> British Association Mathematical Tables (1946), Part-Volume B.

It follows that

$$dv/d\gamma = \int_0^l d\xi/p. \tag{18}$$

To obtain  $dv/d\gamma$  at  $\gamma=0$  we have only to use (16) for  $p$  in the integrand.

**APPROXIMATE SOLUTION**

When the current due to diffusion is very small compared with the current due to the field,  $|dp/d\xi| \ll |\epsilon p|$ , this term can be neglected in (4) and (5) becomes

$$\epsilon^2/2 = \gamma\xi + \text{const.} \tag{19}$$

Denoting the boundary value of electron density at  $\xi=0$  by  $p_0$ , we get

$$\begin{aligned} \epsilon &= [2\gamma\xi + (\gamma/p_0)^2]^{\frac{1}{2}}, \\ p &= \gamma[2\gamma\xi + (\gamma/p_0)^2]^{-\frac{1}{2}}, \\ v &= (\gamma^{\frac{1}{2}}/3)[(2l + (\gamma/p_0^2))^{\frac{3}{2}} - (\gamma/p_0^2)^{\frac{3}{2}}]. \end{aligned} \tag{20}$$

This is essentially the solution given by Mott and Gurney.<sup>11</sup> They also pointed out that for

$$\gamma/p_0^2 \ll 2l \text{ or } \gamma \ll 2lp_0^2, \quad \gamma = (9/8)(v^2/l^3); \tag{21}$$

for

$$\gamma/p_0^2 \gg 2l \text{ or } \gamma \gg 2lp_0^2, \quad \gamma = vp_0/l. \tag{22}$$

We note that the solution contains only one boundary value of  $p$ , i.e., the boundary from which the electrons flow. As is shown in the appendix, for large  $v$  the influence of  $p$  at the end boundary on  $v$  becomes small. The approximate solution will thus be expected to apply for large

$v$ . In fact, comparing (19) and (5) we see that the approximate solution will apply if

$$\epsilon^2 \gg d\epsilon/d\xi. \tag{23}$$

Mott and Gurney taking for the average value  $d\epsilon/d\xi \sim \epsilon/l$  get from (23) the following condition for the applicability of the approximate solution:

$$v \sim l\epsilon \gg 1. \tag{24}$$

This condition may be too lenient since, strictly speaking, (23) should be true for all  $\xi$ . On the other hand, for the assumption and the result of the approximate solution to be consistent, we should have, by substituting (20) into (23),

$$[2\gamma\xi + (\gamma/p_0)^2]^{\frac{3}{2}} \gg \gamma. \tag{25}$$

This will be true for all  $\xi$  if it holds for  $\xi=0$ , i.e.,

$$\gamma \gg p_0^{\frac{3}{2}}. \tag{26}$$

This condition may be too stringent. If  $l$  is not too small, then for very large  $p_0$  (25) may be satisfied for most part of the layer even though (26) is not satisfied. Let us denote  $\gamma c_1 = p_0^{\frac{3}{2}}$  and  $\gamma c_2 = 2lp_0^2$ . Provided (24) is satisfied, we may expect that for  $\gamma < \gamma c_1$  (20) may not be good approximation, for  $\gamma c < \gamma \ll \gamma c_2$  the solution should be closely represented by (21) and for  $\gamma > \gamma c_1$  and  $\gamma \gg \gamma c_2$  the relationship between the current and the potential drop should be very nearly a straight line (22).

**RESULTS OF CALCULATION**

Figures 1 and 2 show the calculated electron density  $p$ , electric intensity  $\epsilon$  and potential drop

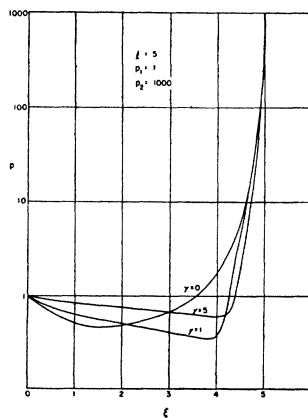


FIG. 1.

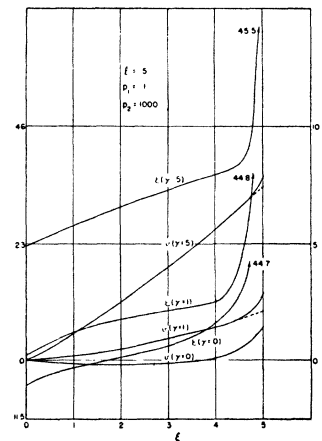


FIG. 2.

<sup>11</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (1940).

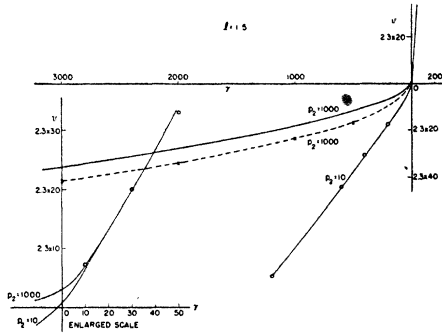


FIG. 3.

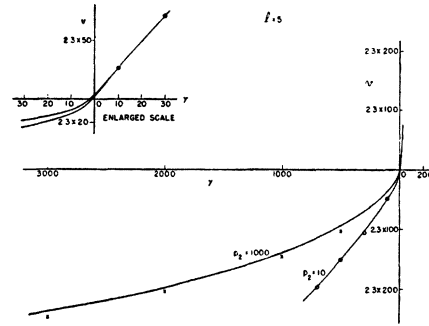


FIG. 4.

$v$  for the equilibrium condition,  $\gamma=0$ , and for two values of current,  $\gamma=1$  and  $\gamma=5$ , flowing in the direction from the boundary of  $p_1=1$  to the boundary  $p_2=1000$ . It is seen that as the current increases, large  $p$ , due to its large value at the boundary toward which the electrons are flowing, is restricted to a smaller and smaller region. For currents in the reverse direction we will have just the opposite situation. For large currents, when the approximate solution becomes justified, the electron density over most part of the layer depends only upon its value at the initial boundary. This is basically the cause of rectification in this model. The field intensity at the initial boundary may be negative for small currents (see curve for  $\gamma=0$ ). It becomes positive for large currents and will increase with current. It will, however, always be the lowest in the whole layer because  $d\epsilon/d\xi = p > 0$ . The sharp rise of  $\epsilon$  at the end boundary is required to balance the large gradient of electron density in this region. Although it may be quite large even at  $\gamma=0$ , it increases very slowly with current. The potential is not greatly affected by the sharp rise of  $\epsilon$  at the end boundary as this is restricted to a small distance.

Figures 3, 4, and 5 show the relationship between current and potential drop in the blocking layer. These curves are calculated for constant  $p_1$  and  $p_2$ . The more correct boundary conditions (1) can be written

$$\begin{aligned} p_1 &= 1 - \gamma \pi b n_{10}^{\frac{1}{2}} (2m/\kappa)^{\frac{1}{2}}, \\ p_2 &= p_{20} + \gamma \pi b n_{10}^{\frac{1}{2}} (2m/\kappa)^{\frac{1}{2}}, \end{aligned} \quad (27)$$

taking  $N=n_{10}$ . When the values of  $n_{10}$  and  $n_{20}$  are known, we have no difficulty in applying these boundary conditions. In the discussion of

copper oxide rectifiers below we shall see when the variations in  $p_1$  and  $p_2$  become important in an actual case. For not too large  $\gamma$  when  $p_1$  and  $p_2$  are approximately constant we have general curves for different values of  $p_2/p_1$  independent of the absolute value of  $n_{10}$ . Curves of Figs. 3-5 are so calculated. They show general characteristics under this approximation. In interpreting these curves it should be borne in mind that the values of  $l$  and  $\gamma$  are relative only since their units depend upon  $n_1$ . The values of  $v$  are definite for a given temperature, its unit being  $kT/e$ . It should also be pointed out that  $v$  is the potential drop across the layer. The applied voltage is  $v_{ap.} = v - v_{\gamma=0}$ . The values of  $v_{\gamma=0}$  is  $\ln(p_2/p_1)$ , thus for  $p_2/p_1=1000$ ,  $v_{\gamma=0}=6.9$ .

It is interesting to compare these curves with the approximate solution (20). The values of  $\gamma c_1$  and  $\gamma c_2$  for these curves are given in Table I. We see from this table that in all three figures the curves for the direction of high resistance

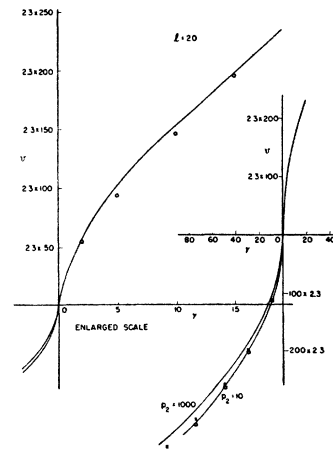


FIG. 5.

TABLE I. Values of  $\gamma c_1$  and  $\gamma c_2$ .

Fig.	Curve	$\gamma c_1$	$\gamma c_2$
3	Direction of high resistance	1	3
	Direction of low resistance $p_2 = 10$	31.6	300
	Direction of low resistance $p_2 = 1000$	31600	$3 \times 10^6$
4	Direction of high resistance	1	10
	Direction of low resistance $p_2 = 10$	31.6	1000
	Direction of low resistance $p_2 = 1000$	31600	$10^7$
5	Direction of high resistance	1	40
	Direction of low resistance $p_2 = 10$	31.6	4000
	Direction of low resistance $p_2 = 1000$	31600	$4 \times 10^7$

should agree well with the approximate solution. The points shown by circles in the enlarged plots are calculated by using (20). We see that they actually check well with the curves. Most of the curves in Figs. 3 and 4 are for  $\gamma > \gamma c_2$ ; they are accordingly approximately straight lines with slopes  $l/p_0 = l$ . The curve in Fig. 5 approximates the square law (21) since it is in the range  $\gamma c_1 < \gamma < \gamma c_2$  for the most part. In the direction of low resistance the approximate solution should hold for the curves  $p_2 = 10$ . Points calculated by using (20) are shown by circles. They do agree well with the curves. According to Table I, solution (20) may not be good approximation for the curves  $p_2 = 1000$ . The points calculated according to (20) are shown by crosses. The agreement with the corresponding curves are not very good. In the case of Fig. 3 the deviation is quite large.

It is interesting to note that according to (22) for sufficiently large currents the ratio of resistances in the two directions becomes  $p_2/p_1$ , independent of  $l$ . But comparison of the calculated curves shows that the larger the thickness the poorer is the rectification at small voltages.

### DISCUSSION

The essential point of our theory is that it takes into account the space charge due to current carrying charge, whereas the fixed space charge is considered negligible in comparison. As pointed out in the introduction, this theory should apply to all artificial blocking layers, at least for sufficiently large currents in the direction of easy flow. A natural blocking layer should disappear with the current approaching infinity (resistance approaching zero) as the applied voltage approaches  $(kT/e) \ln(n_2/n_1)$ ,<sup>2</sup> which is

usually around a few tenths of one volt. Mott's theory of artificial blocking layers,<sup>1</sup> which likewise neglects the free space charge, also predicts that when the voltage applied to the layer in the direction of easy flow approaches  $(kT/e) \ln(n_2/n_1)$ , "the resistance of the contact (layer) should drop to a value comparable with a slab of the semiconductor having the same thickness and should thus be independent of the field." Mott was referring to an artificial blocking layer of the same material as the bulk semiconductor only with fewer impurity centers; i.e., the density of free charge carriers  $n_2$  of the blocking layer at the boundary with the semiconductor is the same as the normal  $n_0$  of the bulk semiconductor. If the layer is of a different material, the  $n_2$  is not necessarily the same as  $n_0$ , but the conclusions of this theory will be essentially the same: when voltage applied in the direction of easy flow approaches  $(kT/e) \ln(n_2/n_1)$  the resistance of the blocking layer should drop to a value corresponding to the normal resistance of a slab of material, with free charge carrier density  $n_2$ , having the same thickness as the layer, and should thus be independent of the field. According to our theory the resistance of the layer should also reach such a stage as is shown by (22), but not necessarily at  $V_{ap.} = (kT/e) \ln(n_2/n_1)$ , which is only a fraction of a volt. Equation (22) becomes valid only when  $\gamma \gg 2lp_0^2$ . In fact, all our curves for  $p_2 = 1000$  in Figs. 3-5 cover ranges of  $\gamma$  far below  $2lp_2^2$ , although the voltages reached are considerably above  $(kT/e) \ln 1000$  (0.175 volt at room temperature); as high

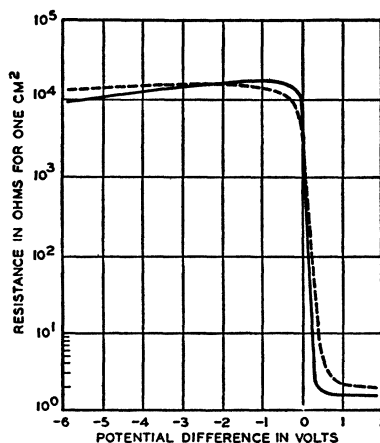


FIG. 6. Dashed line,  $R = V/i$ ; solid line,  $R = dV/di$ .

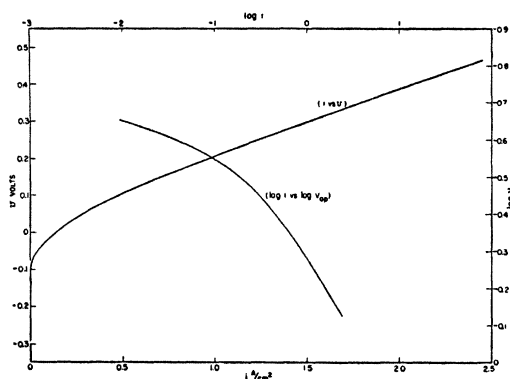


FIG. 7.

as  $800kT/e$  in Fig. 5. This essential difference between the results of our theory and those of previous theories brings out the effect of the free space charge.

Thermionic oxide cathodes with coating consisting of BaO and nickel core containing a small percentage of Si have been found to form a layer of  $Ba_2SiO_4$  between the core and the coating,<sup>3</sup> having a much higher resistivity than the coating. Such a layer exhibits rectification.<sup>12</sup> In the direction of easy flow for voltages as high as several hundred volts across the layer (interface), its resistance continues to decrease. Such behavior cannot be explained by the previous theories but can be understood in the light of our theory.

Copper oxide rectifiers have been found to have a high resistance layer near the contact due smaller concentration of excess oxygen near the contact than in the bulk oxide. This is a case for the application of our theory. Figure 6 reproduces the data given by Brattain.<sup>13</sup> The capacity  $C$  is given to be of the order of  $2 \times 10^{-2}$  microfarad/cm<sup>2</sup>. From this the thickness of the blocking layer can be estimated:

$$L = k/4\pi C = 5.3 \times 10^{-5} \text{ cm,}$$

taking  $\kappa = 12$ .<sup>2</sup> The curve shows that for the direction of high resistance the resistance becomes practically constant for  $V \sim 1$  volt (dashed curve). This, in the light of our theory, is the value given by (22). In terms of ordinary units

$$R_1 = L/ebn_1.$$

<sup>12</sup> W. E. Mutter, Quarterly Progress Report, Research Laboratory of Electronics, M.I.T. (April, 1947).

<sup>13</sup> W. H. Brattain, Bell. Lab. Record 19, 153 (1941).

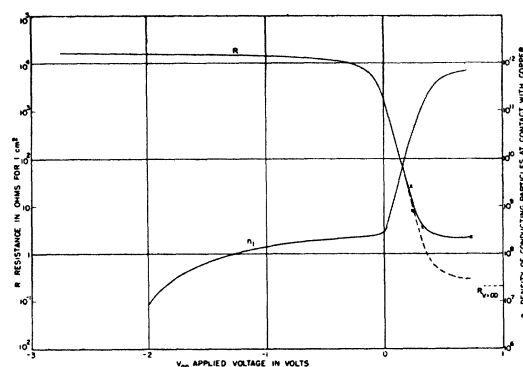


FIG. 8.

Taking  $b = 80 \text{ cm}^2/\text{sec. volt}^1$  and  $R = 1.5 \text{ ohm}$  for one cm<sup>2</sup> from the curve, we get  $n_1 = 2.83 \times 10^8 \text{ cm}^{-3}$  at the contact with copper. The value of  $n_2$  at the other boundary will be the same as that of the bulk oxide, the resistivity of which is given to be of the order  $\rho = 2 \times 10^3 \text{ ohm cm}$ . In terms of units rationalized with respect to  $n_1$  the thickness is  $l = 2.22 \times 10^{-3}$ . We shall take  $n_1 = 3 \times 10^8$  per cm<sup>3</sup>,  $n_2 = 3 \times 10^{13}$  per cm<sup>3</sup> and  $l = 3 \times 10^{-3}$ . These values give  $L = 7.16 \times 10^{-5} \text{ cm}$ ,  $R_1 = 1.87 \times 10^4 \text{ ohm}$  for one cm<sup>2</sup> and  $\rho = 2.98 \times 10^3 \text{ ohm cm}$ .

The resistance at zero applied voltage,  $V_{ap} = 0$ , is calculated by using (18). It comes out to be  $1.63 \times 10^3 \text{ ohm}$  for one cm<sup>2</sup>. Referring to the experimental curve (Fig. 6) we see that this is of the correct order of magnitude. This result is reassuring. The relationship between current and potential drop across the layer for the direction of low resistance is calculated by the rigorous solution (11). Figure 7 gives the calculated curves of  $i$  versus  $V$  and  $\log i$  versus  $\log V$ . It would be interesting to carry the calculation to smaller values of  $i$ , especially for the logarithmic plot. Unfortunately, we are limited by the range of the table of Airy integrals, for the direction of high resistance (20) is used for the calculation. This should be good approximation for the range covered (for  $v > \ln(n_2/n_1)$  or  $V_{ap} > (kT/e) \ln(n_2/n_1) = 0.292 \text{ volt}$ ). Figure 8 gives the semilogarithmic plot of the calculated resistance of the rectifier against the applied voltage. A constant resistance of two ohms per cm<sup>2</sup> corresponding to the resistance of the bulk oxide, as estimated from the experimental curve, is added to the calculated resistance of the layer itself, which,

as shown by the dashed curve, differs appreciably from the total resistance only for large currents in the direction of easy flow. Comparing this curve with the experimental curve (dashed curve in Fig. 6) we see the general satisfactory agreement. In the direction of low resistance, which is the important region for the test of our theory, the calculated curve drops too fast. The previous theories would, however, give an even faster drop, since they make the resistance of the layer drop to the low value  $R_{V=\infty}$  (shown in Fig. 8) at a voltage  $V \sim (kT/e) \ln(n_2/n_1) = 0.292$  volt. In fact, the slope of our calculated curve  $R$  at  $V_{ap.} = 0$  corresponds to

$$d \ln R / dV = (1/1.91)(e/kT),$$

where Mott's theory gives at  $V_{ap.} = 0$

$$d \ln R / dV = e/kT.$$

Thus our theory gives better agreement with experiment than the previous theories. The remaining discrepancy may be due partly to some error in the choice of constants for the calculation. The thickness of the layer is determined from the given representative value of the capacity. The actual value may vary from specimen to specimen. Furthermore, the capacity really gives a measure of only a part of the blocking layer, which has low charge density. Only with sufficient voltage applied in the blocking direction will the low charge density extend to almost the whole of the layer (see Fig. 1). Therefore, depending upon how it is measured, the capacity may correspond to a much smaller thickness than the true thickness of the layer. Still there may be other more fundamental causes for the discrepancy between theory and experiment, such as non-uniformity of the blocking layer as suggested by Mott.<sup>1</sup>

Our curves are calculated for constant  $n_1$  and  $n_2$ . More accurate calculation should take into account their variations according to (1). Actually the current values for the range calculated makes little change in  $n_2$ . But  $n_1$  should change according to the curve shown in Fig. 8. Although in the direction of low resistance  $n_1$  varies greatly, the ratio  $n_2/n_1$  remains sufficiently large for the effect of this variation on the results of calculation to be small. For the direction of high resistance  $n_1$  remains sensibly constant up to

$V_{ap.} \approx 1$  volt. Then it begins to drop. The resistance should then rise steeply. However, as shown by Mott for copper oxide rectifiers with a blocking layer thickness of  $10^{-4}$  cm, the effect of mirror-image force becomes appreciable at applied voltages  $\sim 1$  volt. This effect increases  $n_1$  and decreases the resistance. We shall not go into the effect of the mirror-image force which has been treated in a number of previous works.<sup>14</sup>

Schottky<sup>15</sup> has shown that selenium rectifiers with evaporated electrodes show straight line relationship between  $1/C^2$  and the applied voltage, which indicates according to his theory uniformity of impurity (Störstellen) concentration or the absence of artificial blocking layers. According to the same author selenium rectifiers with electrodes deposited by cathode sputtering have layers (of the order of  $3 \times 10^{-5}$  cm in thickness) of reduced impurity concentration. For such cases our theory should apply, at least when the voltage applied in the forward direction approaches  $(kT/e) \ln(n_2/n_1)$ .

In conclusion we wish to point out that besides the various existing cases of application of our theory, of which copper oxide rectifiers have been discussed in detail, there is the possibility of development of rectifiers with an artificial insulating layer between two good conductors. Such rectifiers should have certain advantages, as pointed out by Torrey and Whitmer (see reference 14, p. 70). Our theory will be helpful for such development.

#### APPENDIX

The functions  $Ai(\theta)$  and  $Bi(\theta)$  are oscillatory for  $\theta < 0$ . Only for  $\theta > 0$  do we get large values of  $v$ . For  $\theta > 0$  the function  $Ai(\theta)$  decreases toward zero and  $Bi(\theta)$  increases continuously. For  $v > 0$  we have

$$Ai(\theta_2) + (B/A)Bi(\theta_2) < Ai(\theta_0) + (B/A)Bi(\theta_0),$$

$$(B/A)[Bi(\theta_2) - Bi(\theta_0)] < Ai(\theta_0) - Ai(\theta_2) < Ai(\theta_0).$$

Since  $Bi(\theta)$  increases very fast with  $\theta$  we have

$$Bi(\theta_2) \gg Bi(\theta_0),$$

$$\therefore (B/A)Bi(\theta_2) < Ai(\theta_0),$$

$$(B/A)Bi(\theta_0) \ll Ai(\theta_0).$$

<sup>14</sup> H. C. Torrey and C. A. Whitmer, *Crystal Rectifiers* (1948).

<sup>15</sup> W. Schottky, *Zeits. f. Physik* **118**, 539 (1942).



Equation (13) can be written:

$$p = 2(R^2 - \theta)[\gamma/2]^{\frac{1}{2}},$$

where

$$R = u'/u.$$

From the condition at the initial boundary  $R_0 \approx Ai'(\theta_0)/Ai(\theta_0)$  can be easily calculated.  $\theta_0$  can be found then from the table. For the end boundary,  $\theta_2 = \theta_0 + l[\gamma/2]^{\frac{1}{2}}$ , we can similarly calculate  $R_2 = u'(\theta_2)/u(\theta_2)$  from  $p_2$ . Since

$$u'(\theta_2)/u(\theta_2) = [Ai'(\theta_2) + (B/A)Bi'(\theta_2)] / [Ai(\theta_2) + (B/A)Bi(\theta_2)],$$

taking the values of  $Ai(\theta_2)$ ,  $Ai'(\theta_2)$ ,  $Bi(\theta_2)$ , and

$Bi'(\theta_2)$  from the table, the value of  $B/A$  is readily calculated. The term involving  $B/A$  is significant only in the immediate neighborhood of the end boundary. It serves to adjust the boundary value of  $p$ . Since it becomes negligible for small values of  $\Delta\theta = \theta_2 - \theta$  a large  $p_2$  results only in a sharp rise of  $p$  near the very boundary. The density of electrons over most of the layer is not much affected by the value of  $p_2$  (all this is for large  $v$ ). The dashed lines joining the curves of  $v$  at the end boundary in Fig. 2 is calculated by neglecting the term involving  $B/A$ . We see that for  $v > 40$  neglecting this term will involve little error.

## On the Theory of Vacancy Diffusion in Alloys

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(Received July 12, 1948)

The theory of diffusion in alloys is discussed on the basis of the migration of lattice vacancies in an attempt to interpret the experiments of W. A. Johnson on diffusion in gold-silver alloys. It is assumed that the lattice network preserves its identity during the diffusion even though there is a resultant vacancy current passing through any region. It is also assumed that two types of atom, designated as  $A$  and  $B$  atoms, are present in the lattice. The diffusion coefficients are expressed in terms of a function  $p(n_{a1}, n_{a2})$  giving the probability that a vacancy in jumping from one atomic plane (designated as plane 2) to a neighboring plane (designated as plane 1) will interchange places with an  $A$  atom if there are  $n_{a1}$   $A$  atoms per unit area of plane 1 and  $n_{a2}$   $A$  atoms in plane 2. It is found that the chemical

diffusion coefficient is related to the function  $p$  in a very different way from the diffusion coefficients for radioactive tracers if the latter migrate when no chemical gradient is present. Models of increasing complexity are employed to derive explicit expressions for the function  $p$ . It is found that Johnson's experiments can be explained only with the use of models that are more complex than those commonly used. The theory of vacancy diffusion is also employed to interpret the experiments of Smigelskas and Kirkendall concerning the relative displacement during diffusion of fiducial markers placed at the interface between copper and brass. An experiment which could provide an absolute test for vacancy diffusion is proposed.

### I. INTRODUCTION

THE experiments of W. A. Johnson<sup>1</sup> on the diffusion in 50-50 gold-silver alloys have raised an interesting question concerning the theory of diffusion in alloys. Johnson investigated the rate at which radioactive silver and gold atoms diffuse in the alloy as well as the rate at which a minor gradient in composition is made uniform. The system studied is rather an ideal one because the constituent atoms combine substitutionally over the entire range of composition in the face-centered cubic system and do

not seem to exhibit the development of long range order at particular compositions, as in the copper-gold system. The specimens on which measurements were made contained planar gradients of the diffusing atoms, so that only one Cartesian variable enters in the diffusion equation.

Figure 1 shows the measured diffusion coefficients when plotted as functions of temperature. As is conventional in the field, the logarithm of the diffusion coefficient is plotted as a function of the reciprocal of the absolute temperature. The upper curve represents  $D_c$ , the diffusion coef-

<sup>1</sup> W. A. Johnson, *Trans. A.I.M.M.E.* **147**, 331 (1942).