of excitation energy and electron affinity means that the extra electron is very loosely bound to the O atom, $E_e(O^-)\cong 2.2$ ev. Thus, the O^- excited state observed here is that which lies very close to the positive energy continuum, the only stable excited state considered possible on theoretical grounds.[38] With one possible exception,[37] placing of the 2.2-ev excitation on the other product in these six processes is clearly impossible within limits of experimental error.

[38] H. S. W. Massey, *Negative Ions* (Cambridge University Press, London, 1950), second edition, p. 20.

The author wishes to express his gratitude to P. W. Anderson, G. H. Wannier, and A. H. White for helpful discussions during the course of the work; to P. W. Anderson, R. E. Fox, N. B. Hannay, and T. Kjeldaas for critical reading of the manuscript; to H. W. Weinhart, under whose supervision the experimental tube was constructed; and to F. J. Koch for technical assistance.

REVIEWS OF MODERN PHYSICS VOLUME 23, NUMBER 3 JULY, 1951

The Copper Oxide Rectifier

WALTER H. BRATTAIN
Bell Telephone Laboratories, Murray Hill, New Jersey

It is shown that the conductivity in the ohmic part of the cuprous oxide layer can be explained with the usual band picture of semiconductors only by assuming the presence of some donor-type impurities in addition to the usual acceptor type. The energy difference between the acceptors and the filled band is 0.3 electron volt, and the total number of impurity atoms is about 10^{14} to 10^{16} per cm^3, the number of donors being less than but of the same order as the number of acceptors. Applying the Schottky theory of the space charge exhaustion layer, one finds from the dependence of capacity of the rectifier on bias voltage that the density of ion charge in the rectifying layer is of the same order of magnitude as the difference between the donors and acceptors found from the conductivity, thus furnishing a check for the theory. The field at the copper-cuprous oxide interface calculated from the space charge is about 2×10^4 volts/cm; the height of the potential at the surface as compared with the oxide interior is about 0.5 volt; and the thickness of the space charge layer about 5.0×10^{-5} cm. The diffusion equation for flow of current through this space charge region can be integrated to give the current in terms of the field at the interface and the applied potential across the space charge layer. Two currents are involved, one from the semiconductor to the metal (I_s) and one from the metal to the semiconductor (I_m) which is similar to a thermionic emission current into the semiconductor. The net current is, of course, $I=I_m-I_s$. One can get this "emission" current (I_m) by dividing the true current by the factor $1-\exp(-eV_a/kT)$, where V_a is the applied potential. This emission current depends on the absolute temperature and on the field at the copper-cuprous oxide interface. At high fields the logarithm of the current is proportional to the square root of the field, and at low fields the current decreases more rapidly indicating a patchy surface having small areas of low potential maximum from which all the emission comes when the field is large. This effective potential maximum measured from the Fermi level in the copper is about 0.5 ev, and the fraction of the total area effective ranges from 10^{-2} to 10^{-5} depending on how the rectifier was made. This last factor—the fraction of the area having this low potential maximum—is by far the most important variable, resulting in low reverse currents when the fraction is small and large reverse currents when the fraction is large.

I. INTRODUCTION

DURING the past few years considerable progress has been made toward an understanding of rectification at a metal-semiconductor contact. Mott[1] has shown that rectification results from a potential barrier at the contact which impedes the flow of current carriers, electrons or holes. The width of the barrier is so large, 1000A or more, that tunneling is relatively unimportant. Electrons must have sufficient thermal energy to surmount the barrier.

Schottky[2] has shown that this barrier, or blocking layer, may be physical rather than chemical in nature. In a physical blocking layer the potential barrier results from a space charge layer in the semiconductor next to the metal and the corresponding induced charge on the metal surface. These two charge distributions form a double layer which adjusts the potential of the semiconductor relative to the metal for equilibrium conditions. The space charge arises from ionized impurity centers. These centers are of the same nature, and may even have the same concentration, as those responsible for the conductivity in the main body of the semiconductor. No change in the chemical constitution of the semiconductor next to the metal is required. If the impurity centers are completely ionized throughout most of the barrier region, Schottky's exhaustion layer theory may be applied. The theory is much simplified for this limiting case, which is the most important one for practical applications.

Mott applied his theory to the copper oxide rectifier. Schottky used the selenium rectifier as his primary example, and he also discussed briefly the application to copper oxide. During the war there was a good deal of work done in this country on the theory of the point

[1] N. F. Mott, Proc. Roy. Soc. (London) **171**, 27 (1939).
[2] W. Schottky, Z. Physik **113**, 367 (1939).

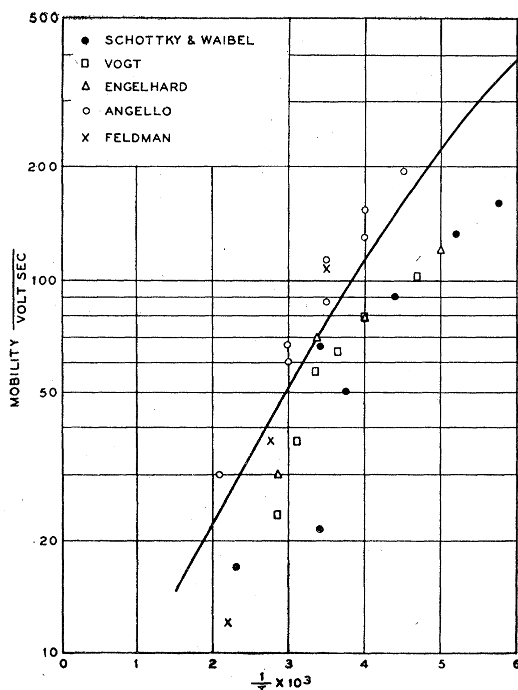

FIG. 1. Mobility of holes in cuprous oxide *vs* the reciprocal of the absolute temperature.

contact rectifiers made with germanium or silicon.[3] It has been found that the Mott-Schottky type of theory gives the main qualitative features of the current voltage characteristic and its dependence on temperature, and also of the variation of capacity of the barrier with the direct bias voltage. There are, however, several quantitative discrepancies which have usually been attributed to a patch effect; that is, to a non-uniformity of the barrier over the contact area.

A large amount of data have been accumulated, mostly prior to the war, in connection with the development of copper oxide rectifiers at the Bell Telephone Laboratories.[4] The purpose of the present investigation is to make an analysis of these data in the light of the Schottky exhaustion layer theory. Capacity and temperature data are used to estimate the height and width of the potential barrier, and the concentration of impurity centers. These, in turn, are used to interpret the current voltage characteristic. It is again found that some sort of patch theory is required. Our main conclusions in regard to the potential barrier are in agreement with those of Mott, although he did not attempt to correlate his results with impurity concentration. This paper is confined to a discussion of the dc or low frequency characteristics. Bardeen has considered the the variation of impedance with frequency in another paper.[5]

[3] H. C. Torrey and C. A. Whitmer, *Crystal Rectifiers* (McGraw-Hill Book Company, Inc., New York, 1948).
[4] W. H. Brattain, Bell Labs. Record **19**, 153 (1941).
[5] J. Bardeen, Bell System Tech. J. **28**, 428 (1948).

The investigation naturally divides itself into three parts: I. An analysis of the conductivity in the body of the oxide layer to determine the concentration and energy of the impurity centers; II. An analysis of the junction capacity and of its dependence on applied bias voltage to determine the barrier height and the concentration of impurity centers in the barrier region; III. An analysis of the dc current characteristic and of its dependence on temperature.

Copper oxide is a defect semiconductor. The carriers are missing electrons, or holes, in the filled band. The main impurity centers, acceptors in this case, are probably vacant copper ion lattice sites. These are analogous to F-centers in alkali halide crystals. The neutral center corresponds to a hole localized at the vacant site. There is evidence from the variation of concentration of holes with temperature that there must be donors as well as acceptors present. The nature of the donors is unknown.

The mean free path of holes in copper oxide is the order of 5×10^{-7} cm, which is small compared with the thickness of the barrier. Thus the diffusion theory rather than the diode theory is used to obtain the current voltage characteristic. The expression for the current involves the applied potential, the barrier height, the electrostatic field in the semiconductor at the metal contact, and the mobility of the carrier. In the diode theory, the current in the reverse direction can be interpreted as the thermionic emission current from the metal into the semiconductor. In the diffusion theory, the current does not have so simple an interpretation, but the barrier height enters in the same way in both. The Schottky effect[6] at high fields and the effect of patches on the current is the same in both theories. This leads to an analysis of the current voltage characteristic by methods similar to those used for the current from a thermionic emitter with a patchy surface. An important parameter determining the current is the ratio of the area of the low potential maximum to the total contact area.

Data are analyzed for copper oxide units which were chosen to illustrate the known empirical variations that can be obtained from heat treatment and from different sources of copper. Each unit on which detailed data were obtained was chosen as typical of a lot of similarly prepared units. Copper oxide rectifiers, made from the same copper and to all intents and purposes in the same way, will show considerable spread. Any unit picked at random may not be typical of the group. Care was taken to obtain some data on a number of similarly prepared units before picking out one as typical.

The methods of analysis are described in Sections I, II, and III, and are illustrated by application to data on one or two individual rectifiers. In part IV, results are given for all units analyzed and are discussed in terms of the patch theory.

[6] W. Schottky, Physik. Z. **15**, 872 (1914).

II. CONDUCTIVITY

Cuprous oxide is an impurity semiconductor; therefore, the conductivity of a sample depends on its history. The conductivity may be expressed in the form

$$\sigma = nev,$$

where n is the concentration of carriers, in this case holes in the filled band, e is the magnitude of the electronic charge, and v is the mobility. The mobility of holes in Cu_2O is determined by lattice scattering and so is independent of impurity concentration. Differences in conductivity among different samples are due to differences in n, the concentration of holes. Information on the concentration and energy of impurity levels can be obtained from the variation of n with temperature. The latter can be obtained from the conductivity, if the mobility and its variation with temperature are known.

The mobility can be obtained from the product of the Hall coefficient, R, and the conductivity, σ. Hall measurements on Cu_2O have been made by a number of observers. Although the conductivities of the different samples differ widely, the mobilities agree quite well considering the difficulties involved in the measurement and in getting homogeneous samples. In Fig. 1, values of $R\sigma$ are plotted as a function of $1/T$. Each of the points of Vogt,[7] Engelhard,[8] Angello,[9] Feldman,[10] and Schottky and Waibel[11] are averages of a number of samples. Angello's values are a little higher than those of most of the other observers. For converting conductivities to concentrations, we adopt the line which corresponds to the function

$$v = A(e^{\theta/T} - 1),$$

with $A = 10.5$ and $\theta = 665°$. This function, plotted in Fig. 1, gives more weight to Angello's values than to the others. The exact choice of mobility does not have a critical bearing on the analysis we will make.

Fröhlich and Mott[12] have derived a theoretical expression of this form based on scattering by longitudinal polarization waves. The characteristic temperature, θ, is that of waves of long wavelength (the frequency is $k\theta/h$). The multiplying factor A involves the characteristic temperature and the effective mass of the carriers. If the effective mass is taken equal to the ordinary electron mass, the theoretical value of A is the order of 5 to 10. The characteristic temperature is unknown. The empirical value of 665° is not unreasonable. In attempting to fit Engelhard's data at lower temperatures by an expression of this form, Fröhlich and Mott obtained a smaller value for θ and a larger value for A. We believe that our values are more reasonable, and that something other than longitudinal polarization waves contribute to the scattering below 200°K.

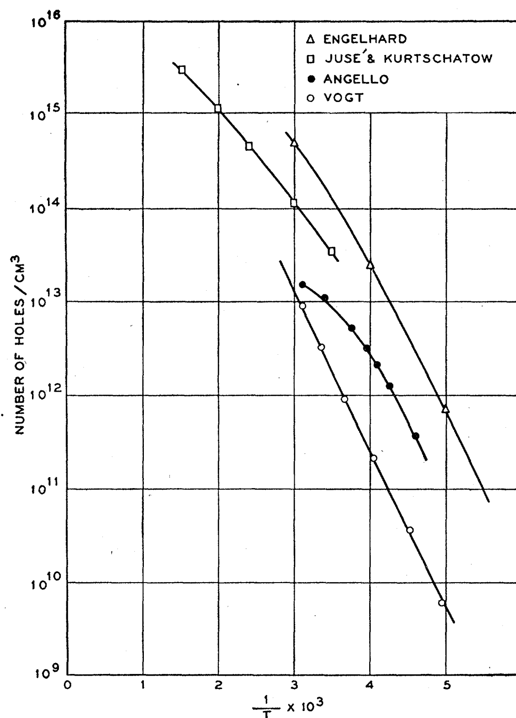

FIG. 2. Typical results of the variation of hole concentration in cuprous oxide *vs* the reciprocal of the absolute temperature.

The variation of n, and thus of σ, with temperature is a structure sensitive property, and seemingly discordant results have been obtained by different observers. We believe that most results can be explained if it is assumed that there are donor as well as acceptor levels in Cu_2O. Before discussing the conductivity of the oxide layer in the rectifier, we shall review briefly the results of the various investigators on supposedly homogeneous samples of the oxide. Typical results on the variation of concentration with temperature are shown in Fig. 2. The values were obtained either directly from Hall measurements or from the conductivity by using the average mobilities from Fig. 1.

A plot of log n *versus* $1/T$ should give a straight line if n varies as

$$n = \text{const } e^{-\epsilon/kT}. \tag{1}$$

All curves of Fig. 2 are approximately parallel at low temperatures, the slope corresponding to an energy ϵ of about 0.3 ev. The measurements of Vogt and of Engelhard, made mostly below room temperature, give straight lines with this slope. The measurements of Jusé and Kurtschatow,[13] made at room temperature and above, plot in lines with about half this slope, but in some cases there is evidence for an increasing slope

[7] V. W. Vogt, Ann. Physik 7, 183 (1930).
[8] E. Engelhard, Ann. Physik 17, 501 (1933).
[9] S. J. Angello, Phys. Rev. 62, 371 (1942).
[10] W. Feldman, Phys. Rev. 64, 113 (1943).
[11] W. Schottky and F. Waibel, Physik. Z. 34, 858 (1933).
[12] H. Fröhlich and N. F. Mott, Proc. Roy. Soc. (London) 171, 496 (1939); H. Fröhlich *et al.* Phil. Mag. 41, 221 (1950).
[13] W. P. Jusé and B. W. Kurtschatow, Physik. Z. Sowjetunion 2, 453 (1933).

near room temperature. The measurements of Angello do not give straight lines. There is a knee a little below room temperature. The low temperature slope appears to be approaching that corresponding to $\epsilon=0.3$ ev.

The relationship between the activation energy ϵ derived from the conductivity or Hall coefficient and the ionization energy E of an impurity center has been discussed by a number of authors. In the case of Cu_2O, it is possible that of the total number of acceptors, N_A, a part, N_D, are occupied by electrons from higher lying donor levels. The remainder, N_A-N_D, are available for ionization by electrons from the filled band. Thus

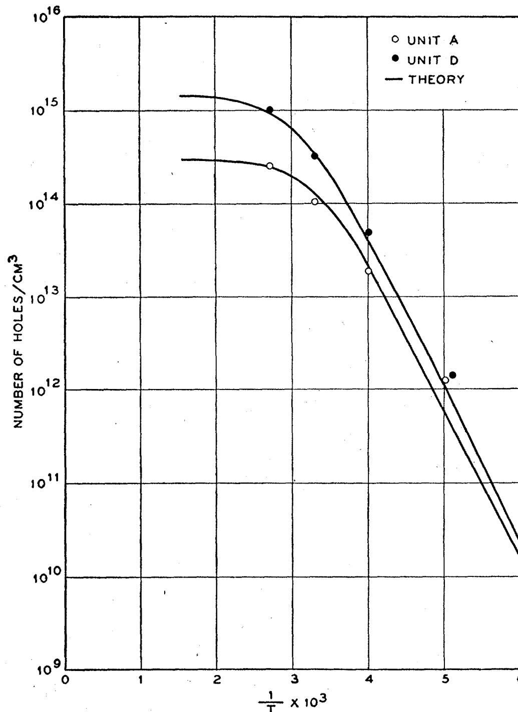

FIG. 3. Hole concentration for cuprous oxide layers on copper.

at temperature T there are n holes in the filled band, N_D+n negatively charged acceptors, N_A-N_D-n neutral acceptors, and N_D positively charged donors (positive ions in the lattice). The statistics for this situation have been discussed by deBoer and vanGeel,[14] and have been applied by Nijboer[15] to other examples. If E is the energy required to ionize a neutral acceptor to form a negative ion and hole, the law of mass action gives

$$[n(N_D+n)]/(N_A-N_D-n)=Ae^{-E/kT}, \qquad (2)$$

where A is the constant:

$$A=(2\pi mkT/h^2)^{\frac{3}{2}}.$$

Equation (2) is a quadratic equation which may readily be solved for n. Certain limiting cases are of interest. First consider the case of low temperatures, where $n\ll N_A-N_D$. If also $n\gg n_D$ (negligible concentration of donors),

$$n=(AN_A)^{\frac{1}{2}}e^{-E/2kT}. \qquad (3)$$

On the other hand, if $n\ll N_D$,

$$n=[(N_A-N_D)/N_D]Ae^{-E/kT}. \qquad (4)$$

Unless $N_D=0$, this situation will prevail at sufficiently low temperatures. At high temperatures, n approaches the limiting value,

$$n=N_A-N_D. \qquad (5)$$

The value ϵ deduced from the variation of n with T at low temperatures may be either E or $E/2$ depending on whether or not donors are present. If donors are present, the slope may decrease from that given by E to that given by $E/2$ as n increases above N_D. The temperature range over which the slope is $E/2$ will be small unless $N_D\ll N_A$.

The data of Fig. 2 can be interpreted in a general way on the basis of this picture. The slope at low temperatures corresponds to $\epsilon=E$, according to Eq. (4). The ratio N_D/N_A required varies from about 0.05 to about 0.95. The saturation number of holes, N_A-N_D, is of the order of 10^{14} or 10^{15} for Angello's samples and somewhat larger for the others.

The conductivity of the oxide layer in a number of rectifiers has been obtained from the limiting ohmic resistance in the forward direction. By using the mobility from the solid curve of Fig. 1, the variation of concentration with temperature has been deduced. Figure 3 gives a plot of log n *versus* $1/T$ for a layer of oxide formed on "Chile" copper unit A and another layer formed on "Oxygen Free High Conductivity" (O.F.H.C.) copper unit D. These data are typical of all oxide layers we have measured, whether on copper or completely oxidized. The curves have a slope at low temperatures corresponding to $\epsilon=E=0.3$ ev, with a tendency to saturate at higher temperatures. There is no appreciable temperature range for which Eq. (3) with $\epsilon=E/2$ is valid.

In order for Eq. (3) to represent the data at low temperatures, the density of acceptors, N_A, would have to be about $10^{20}/cm^3$. Not only is this value unreasonably large, but if it were this large one would certainly expect the number of holes, n, to increase with temperature and without saturation effects until n reaches this same order of magnitude. From Fig. 3 it is evident that the saturation value of n is the order of $10^{16}/cm^3$ and that a satisfactory explanation of the data cannot be obtained if it is assumed that $N_D=0$.

On the assumption that Eq. (4) is the proper one to use at low temperatures, one can determine E and $(N_A-N_D)/N_D$ from the slope and position of the line representing log n. The apparent saturation value at high temperatures gives N_A-N_D. Combining these results, N_A and N_D can be obtained. The solid curves

[14] J. H. deBoer and W. C. vanGeel, Physica **2**, 286 (1935).
[15] B. R. A. Nijboer, Proc. Phys. Soc. (London) **51**, 575 (1939).

of Fig. 3 have been computed from the solution of Eq. (2) to fit the two sets of experimental data. The energy $E=0.3$ ev for both cases; $N_A=4.0\times10^{14}$ and $N_D=1.0\times10^{14}/\text{cm}^3$ for the oxide on Chile copper, and $N_A=20\times10^{14}$ and $N_D=5.0\times10^{14}/\text{cm}^3$ for the oxide on O.F.H.C. copper.

It should be emphasized that these estimates are not reliable except as to order of magnitude. In calculating the value of A, we have assumed the mass to be that of a free electron. Furthermore, in the derivation of Eq. (2), changes in entropy of the lattice vibrations when impurity centers are ionized and other secondary effects have been neglected. Such corrections might change A by a factor of two or three or perhaps more.

Probably, even more important is the fact that the conductivity of the oxide may not be uniform throughout the layer.[16] There is evidence, at least for thicker oxide films, of an increase in conductivity with depth in the oxide layer, the conductivity being greatest for the oxide nearest the mother copper. It has been hard to understand this, since the acceptor levels are thought to be copper defects in the cuprous oxide lattice[17] and the density of these defects should be smaller near the copper and greater near the outside face of the oxide. Now, however, the presence of the donor impurities enables one to explain the variation in conductivity on the assumption that both N_A and N_D decrease as the copper is approached but in such a way that N_A-N_D increases. Since the conductivity, and therefore the density of holes, is not constant in the layer of cuprous oxide, the values of N_A and N_D calculated for a particular oxide layer should be taken only as estimates of the order of magnitude.

Some conductivity measurements on completely oxidized strips have been analyzed as above. Such strips are also non-uniform, the conductivity increasing parallel to the direction of oxidation as one approaches the place where the copper last disappeared. By measuring the conductivity parallel to the direction of growth of the oxide one gets values characteristic of the high resistance part, and by measuring normal to this direction the values are characteristic of the low resistance part. In Fig. 4 the number of holes *versus* the reciprocal of absolute temperature is shown for both cases on one sample. The points are calculated from the experimental data on conductivity, and the solid curves are calculated from Eq. (3). The value of E was 0.3 ev; for the parallel case $N_A=360\times10^{14}$, $N_D=350\times10^{14}$, and for the normal case $N_A=43\times10^{14}$ and $N_D=23\times10^{14}$. While these values are only approximate for the reasons already stated, they do give a good illustration of a case where the number of acceptors apparently decreased as it approached the region where the copper last disappeared but the conductivity nevertheless increased because the donors decreased faster resulting in a larger difference N_A-N_D on the inside than on the outside.

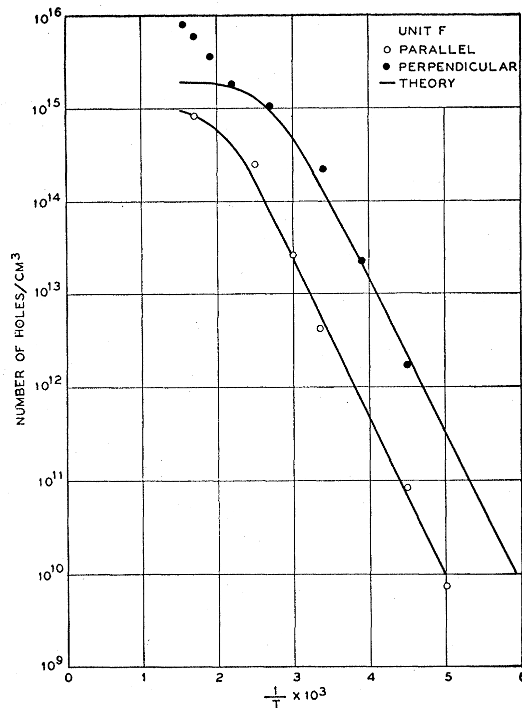

Fig. 4. Hole concentration for different parts of a single sheet of cuprous oxide.

III. THE SPACE CHARGE LAYER

Schottky[2] has shown that from the way the capacity of the junction varies with dc bias voltage it is possible to determine the ionic charge density in the space charge layer. Schottky's picture of the space charge layer, as applied to the copper oxide rectifier, is shown in Fig. 5. It is an energy level diagram, with energy of the electrons increasing upward. The diagram is drawn for the equilibrium condition with no applied voltage. The copper is on the left, the oxide on the right. In order of increasing energy there is in the oxide first the filled band, normally occupied by the valence electrons responsible for bonding the crystal together,

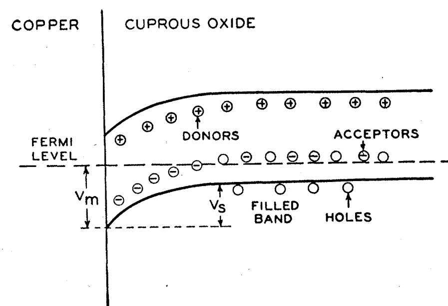

Fig. 5. The space charge layer at the copper-cuprous oxide contact, after Schottky.

[16] W. H. Brattain, Phys. Rev. **45**, 745 (1934).
[17] Bardeen, Brattain, and Shockley, J. Chem. Phys. **14**, 714 (1946).

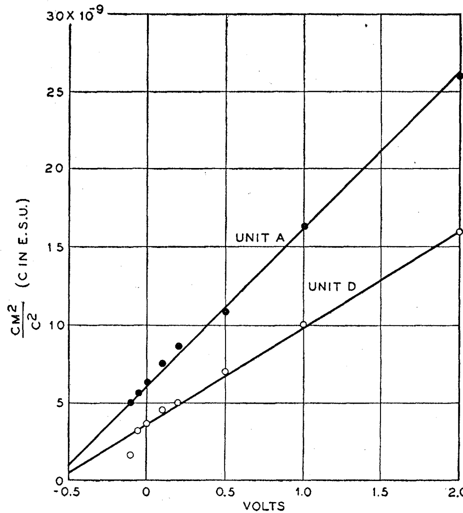

FIG. 6. Change in capacity at copper-cuprous oxide contact *vs* applied potential, after Schottky.

then the "forbidden" band, in which there are no levels in the ideal crystal, and then another continuous band of levels, normally unoccupied, which is called the conduction band. The energy gap, determined from the slope of the intrinsic conductivity line, is about 1.4 ev. The acceptor levels lie in the forbidden band about 0.3 ev above the top of the filled band. They are neutral when vacant and negatively charged when occupied by electrons. The donor levels lie higher in the forbidden band. They are positively charged when vacant, neutral when occupied. At room temperature, the Fermi level runs a little below the level of the acceptors. Levels with energies above the Fermi level are more probably vacant, those with energies below the Fermi level more probably occupied. In the main body of the oxide, most acceptors are neutral. Some have become charged by capture of electrons from the higher donor levels, others have become charged by thermal excitation of electrons from the filled band. The conductivity is due to the vacant levels or holes in the filled band.

There is a drop in electrostatic potential energy in the space charge layer next to the metal. There are very few holes, and practically all acceptors are occupied in the space charge layer, giving a net negative charge density

$$\rho = -e(N_A - N_D). \tag{6}$$

It is this charge, together with the induced charge of opposite sign on the metal surface, which gives the change in potential in the space charge layer.

The energy eV_m is that required to take an electron from the top of the filled band of the oxide and place it at the Fermi level of the metal. The thickness of the space charge layer is such as to give an over-all energy drop across the space charge layer equal to the difference between eV_m and ζ the height of the Fermi level above the filled band in the body of the oxide

$$eV_s = eV_m - \zeta. \tag{7}$$

If a voltage is applied to the rectifier, the drop across the layer is changed from V_s to $V_a + V_s$. Here V_a is the applied voltage corrected for the IR drop in the body of the oxide layer.

Schottky's[2] exhaustion layer theory, in its simplest form, is based on the assumption that the charge density is uniform throughout the space charge layer and equal to that given by Eq. (6). The thickness of the reserve region, or transition region in which the charge density is increasing from 0 to the constant value, is assumed small compared with the total thickness of the layer. If l is the effective thickness of the layer, integration of Poisson's equation gives for the total drop across the layer

$$V_s + V_a = 2\pi\rho l^2/K, \tag{8}$$

where K is the dielectric constant. The capacity of the junction per unit area of contact is simply that of a parallel plate condenser of thickness l and dielectric constant K,

$$C = K/4\pi l. \tag{9}$$

Thus, substituting for l in Eq. (8),

$$V_s + V_a = K\rho/8\pi C^2. \tag{10}$$

The capacity is measured by superimposing a small alternating voltage on the direct bias voltage, V_a. If the concentration of impurity centers in the space charge region is uniform, the thickness of the space charge layer, l, and the capacity C change with applied voltage in accordance with Eqs. (8) and (10). Schottky plots $1/C^2$ as a function of V_a. Equation (10) indicates that such a plot should be a straight line with a slope inversely proportional to the density and with an intercept equal to V_s. Schottky[2] has shown that if the concentration is not uniform, and the plot is not a straight line, the slope is related to the density of charge at the semiconductor end of the space charge layer by the equation

$$\frac{1}{\rho} = \frac{K}{8\pi}\frac{d(1/C^2)}{dV_a}. \tag{11}$$

Schottky plots have been made for the series of rectifiers discussed in the introduction. Plots for two typical rectifiers, units A and D, are shown in Fig. 6. The measured points give approximately straight lines from zero to about two volts bias in the reverse direction. The intercept is the same for both, about 0.55 v. For the calculation of the concentration of ions from the slope, a dielectric constant of 10 was assumed. Values obtained for the ionic density, $N_A - N_D$, are 1.7×10^{15} for unit A and 2.8×10^{15} for unit D. From these values, it follows that the thickness of the space charge layers

at zero bias are 6.3×10^{-5} and 4.8×10^{-5} cm, respectively. The field at the interface, calculated from

$$F=4\pi\rho l/K, \qquad (12)$$

is about 2×10^4 v/cm for unit A and 2.5×10^4 v/cm for unit D.

The corresponding values for N_A-N_D, deduced from the conductivity of the oxide layer, are 3×10^{14} for unit A and 10^{15} for unit D. These are of the order of $\frac{1}{3}$ of those found for space charge layer from the Schottky plot. The agreement as to order of magnitude is probably all that can be expected. There is evidence for an increase in conductivity and thus in N_A-N_D toward the metal junction. Similar values for other copper oxide rectifiers are shown in Table I in the summary.

IV. THE CURRENT VOLTAGE CHARACTERISTIC

The diffusion rather than the diode equations should be used to obtained the current voltage characteristic, since the mean free path of holes in Cu_2O, which is about 5×10^{-7} cm, is small compared with the thickness of the space charge layer, which is about 5×10^{-5} cm. The current is the sum of a conduction current and a diffusion current,

$$I=nevF-vkT(\partial n/\partial x). \qquad (13)$$

Both the field strength, F, and the hole concentration, n, depend on the position in the space charge layer. They are related by poisson's equation for the layer. Integrals of Eq. (13) have been obtained by Mott,[1] Schottky,[2] and Davydov.[18] Mott assumed F constant throughout the layer. Mott's solution, however, applies more generally, because the important part of the barrier, as far as the current voltage characteristic is concerned, is that near the metal interface, and F is approximately constant in this region.

An approximate general solution of Eq. (13), including the effect of the image force near the interface, may be written in the form

$$I=AevF_m(\pi^2F_me^3/4K(kT)^2)^{\frac{1}{4}} \times\exp\{-(e/kT)[V_m-(eF_m/K)^{\frac{1}{2}}]\} \times[1-\exp(-eV/kT)], \qquad (14)$$

where I = current density, $A=2(2\pi mkT/h^2)^{\frac{3}{2}}$, F_m = electrostatic field in the oxide at the metal interface, K = dielectric constant, eV_m = height of the potential barrier at the interface above the Fermi level in the metal, V_a = applied voltage, taken positive in the reverse direction. The solution applies when the height of the barrier, as seen from the semiconductor, is large compared with kT. This will be the case for voltages in the reverse direction and also for small voltages in the forward direction. The effect of the voltage drop due to series resistance in the body of the oxide is not included. Strictly, V_a is the drop across the barrier rather than the applied voltage. The quantity under the fourth root sign is approximately equal to unity, and we neglect this factor except to include the dependence on absolute temperature indicated.*

The exhaustion layer theory is used to relate F_m with V_a;

$$F_m=F_0(1+V_a/V_s)^{\frac{1}{2}}. \qquad (15)$$

Here F_0 is the field at the interface for the equilibrium barrier where no voltage is applied.

There are several ways of comparing Eq. (14) with the experimental results for a copper oxide rectifier. The current voltage characteristic for unit A is shown by the circles in Fig. 7. If one assumes that the copper-cuprous oxide interface is uniform and substitutes in Eq. (14) the values of F_0 and $V_m=(V_s+0.3)$ deduced from capacity measurements, the currents calculated are several orders of magnitude too small in the reverse direction and for small values of V_a in the forward direction. If, on the other hand, one makes the assumption that most of the current flows through small patches of lower potential maximum V_m', then one can obtain a reasonable fit as to order of magnitude. This result is shown in Fig. 7 by the solid curve marked theory. The justification for this last assumption is based on the following analysis.

The current I_m, defined by

$$I_m=\frac{I}{1-\exp(-eV_a/kT)}, \qquad (16)$$

is always of the same sign. According to Eq. (14), I_m varies with V_m and F_m in a similar way to the thermionic emission current from a metal with work function eV_m under an applied field F_m/K. This suggests the follow-

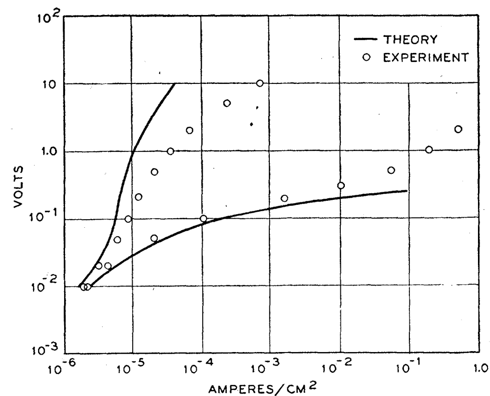

FIG. 7. Comparison of the experimental current voltage characteristic for unit A with theory.

[18] B. Davydov, J. Phys. (U.S.S.R.) 1, 167 (1939).

* *Note added in proof:* The factor $(\pi^2Fme^3/4K(kT)^2)^{\frac{1}{4}}$ is upside down in Eq. (14). This error occurred before the analysis was made. The only effect of this error is to change the argument of the logarithm in Eq. (18) by the factor $T/300$. This would change the points in Fig. 9 slightly. The difference is very small and the effect on the analysis insignificant.

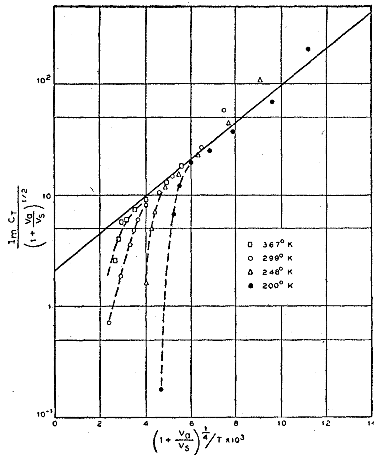

FIG. 8. "Schottky emission" plots for unit A.

ing procedure for analysis of the current voltage characteristic: take the experimental value of I_m and plot $\log[I_m/(1+V_a/V_s)^{\frac{1}{2}}]$ *versus* $F_m^{\frac{1}{2}}$, or its equivalent, namely $(1+V_a/V_s)^{\frac{1}{4}}$. Such a plot is shown in Fig. 8. Actually, this plot shows data at several different temperatures. To make the data at all temperatures comparable, we have multiplied the values of current for each temperature by a constant. This constant (C_T) is different for each different temperature, and we have plotted the values of

$$\log\frac{I_m C_T}{(1+V_a/V_s)^{\frac{1}{2}}} \; versus \; \frac{(1+V_a/V_s)^{\frac{1}{4}}}{T}$$

as suggested by Eq. (14). It is evident from the Fig. 8 that it is possible to choose values of C_T for each temperature so the data at all temperatures do fit together

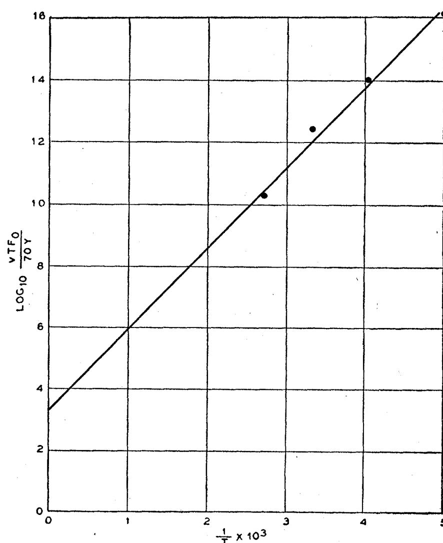

FIG. 9. "Emission current" *vs* the reciprocal of the absolute temperature, unit A.

well, at least at the larger values of the field F_m. This type of plot is analogous to similar "Schottky emission"[6] plots made for thermionic cathodes. The deviations from the straight line at small values of F_m would, in the thermionic case, be considered as very good evidence for a surface of non-uniform work function—in other words, a surface having a patch work effect, i.e., small areas of low work function interlaced with small areas of high work function.[19] The fact that the lower temperature data tend to deviate from the straight line at higher values of the field than the higher temperature data is consistent with the patch theory. The slope of the straight line part should from Eq. (14) have the value $(e^3F_0/k^2K)^{\frac{1}{4}}$. On the basis of the value of F_0 derived from the capacity data the slope should be 163, whereas the actual slope in Fig. 8 is 280. A higher slope than predicted is also characteristic of thermionic surfaces known to be patchy. Another effect that may be partly responsible for this high slope is that at high voltages in the reverse direction the current tends to increase with time in copper oxide rectifiers, and because of this effect the currents at high fields are progressively larger than the instantaneous values, due to the time involved in making the measurements.

The next step is to see if the constants C_T used to adjust for the different temperatures are consistent with Eq. (14). If, for convenience, we take the ordinate for $F_m=0$,

$$\left[\log\frac{I_m}{(1+V_a/V_s)^{\frac{1}{2}}}\right]_{F_m=0} = \log Y; \qquad (17)$$

then from Eq. (14)

$$V_m = (2.3T/11600)\log(vTF_0/70Y). \qquad (18)$$

From the values of C_T and the extrapolated intercept in Fig. 8, we can calculate Y and make the plot suggested by Eq. (18), namely, $\log vTF_0/70Y$ *versus* $1/T$. Such a plot is shown in Fig. 9, which is analogous to a thermionic emission plot of $\log I$ *versus* $1/T$. It is seen that the points do lie approximately on a straight line. The intercept, however, is not at zero as suggested by Eq. (18). The value of the intercept is approximately 3.0, meaning that the value of A in Eq. (12) is 1000 times too large to fit the experimental data. This result could be explained in two alternate ways. Such a deviation from the theoretical intercept could be interpreted as a temperature coefficient of the quantity V_m amounting to 6×10^{-4} ev/degree, which is larger than would be expected on theoretical grounds. The alternate explanation is that the surface is patchy and that the straight part of the plot in Fig. 8 is the result of the emission from patches of work function V_m'. The appropriate parameters, to be used in Eq. (14), are therefore the area of these patches and the potential maximum V_m' rather than V_m and the area of the whole surface. As

[19] J. A. Becker, Revs. Modern Phys. 7, 95 (1935).

TABLE I.

Unit No.	*A*	*B*	*C*	*D*	*E*	F_P	F_N
			History				
Copper	Chile	Chile	03% Tl	O.F.H.C.	Chile	Chile	
High temp.	980°C	1000°C	1000°C	1000°C	975°C	1000°C	
Time	20 min	10 min	10 min	10 min	25 min	180 min	
Low temp.	480°C	600°C	550°C	550°C	490°C	500°C	
Time	3 min	3 min	7 min	7 min	5 min	3 min	
Quench	Water	Water	Water	Water	Air	Air	
			Conductivity				
N_A/cm³	4.0	4.0	4.0	20		360	43×10^{14}
N_D/cm³	1.0	1.0	1.0	5		350	23×10^{14}
N_A-N_D/cm³	3.0	3.0	3.0	15	1.0	10	20×10^{14}
			Capacity				
N_I/cm³	17	17	16	28	3.3	14×10^{14}	
F_0 volts/cm	2.0	1.7	2.5	2.5	0.7	0.5×10^{4}	
l cm	6.3	5.4	8.5	4.8	12	2.0×10^{-5}	
V_s volts	0.58	0.45	1.00	0.58	0.48	0.05	
			I_m				
V_m volts	0.74	0.68	0.80	0.71	0.76	0.64	
V_m' volts	0.54	0.46	0.47	0.58	0.52		
α	10^{-3}	10^{-4}	10^{-5}	10^{-2}	10^{-4}		
Theor. slope	163	152	185	185	100	83	
Exp. slope	280	400	245	520	670	400	

already mentioned, this is the way the curve marked theory in Fig. 7 was calculated. The experimental current in the reverse direction is larger than predicted, chiefly because the experimental Schottky slope is larger than the theoretical slope. In the forward direction the experimental current is less than the predicted current, because at low fields most of the current flows over a potential hill larger than V_m' (patch effect).

On the basis of the above reasoning, it seems reasonable to say that Eq. (14) and some kind of a patch effect at the copper-cuprous oxide interface is a sufficient explanation of the current voltage characteristic of the copper oxide rectifier.

SUMMARY AND CONCLUSION

To summarize the work, the various constants that can be calculated from the analysis are shown in Table I for all of the units for which sufficient data were taken to enable the analysis to be made. Also included in the table are some of the pertinent data regarding the processing of each unit. The source of the copper, the oxidizing temperature and time, the annealing temperature and time, and the type of quench are given.

Reference 4 gives considerable detail on the processing of copper oxide rectifiers and some generalizations on how the various parameters of processing affect the final result. Units *A*, *B*, and *C* were selected from each of large lots of over 100 units, each lot being one furnace batch. *A* and *B* were from batches made over a year apart, and any differences between them are probably due as much to the fact that they were made from different lots of "Chile" copper as to the slight differences in heat treatment. Unit *C* was made from Chile copper with 0.3 percent Tl added. Unit *D* was made from a commercial copper called "Oxygen Free High Conductivity" copper. Unit *E* was different from the rest in that it was quenched in air instead of water. For units of this type the current in the forward direction never really becomes proportional to the applied voltage, so its not possible to assign a true conductivity to the oxide layer. A rough estimate was made however of N_A-N_D. Unit *F* was a thin square of completely oxidized copper. The two values of constants deduced from the conductivity for this sample are those obtained by measuring the conductivity parallel and normal to the growth of the oxide layer, as mentioned in Section I. Here one must not give too much consideration to the fact that these oxide squares were air quenched, since it has been found that when all the copper has been oxidized the method of cooling has very little effect on the resulting resistance of the square. Later, an aluminum layer was evaporated on the polished and etched face of several of these oxide squares resulting in rectifiers. The complete analysis could not be made for this rectifier, because the current voltage characteristic has, so far, been determined only at one temperature.

Table I should be examined first for internal agreement. The ion density in the space charge layer should be equal to the difference between the density of the acceptors and of the donors. If the density of acceptors and donors was constant throughout the oxide layer, then N_A-N_D/cm³ should be equal to N_I/cm³ for each unit. Since the value of N_I/cm³ is dependent on the

assumed value of the dielectric constant and N_A-N_D/cm^3 is only an estimate, as already mentioned, the agreement is probably as good as one could expect. For the unit F, the value of N_I/cm^3 lies between the two estimates of N_A-N_D/cm^3 obtained for F_P and F_n. The potential maximum V_s measured from the top of the conduction band should be equal to the potential maximum V_m measured from the Fermi level in the metal minus the difference between the top of the filled band and the Fermi level, approximately 0.3 volt. One would not expect this relation to hold for a patchy surface for the following reason. For the case of a non-uniform or patchy surface the values given in the table for the potential maximum are averages. For V_s deduced from capacity data, this average is weighted in favor of the potential maximum of those parts of the surface having the largest area, whereas for V_m, deduced from I_m, the average is weighted in favor of those areas having the smallest value of the potential maximum. One would expect, therefore, that $V_s+0.3$ would always be greater than V_m, and this is the case, except for the unit F_P. The last two rows under I_m compare the theoretical and experimental Schottky emission slopes. The experimental slopes are higher than predicted by a factor of 2 to 3. If a lower value of dielectric constant had been used, this disagreement would be less, but the ion density N_I would thereby be increased making the discrepancy between N_I and N_A-N_D larger. It appears that the only factors which may explain this discrepancy are the following: First the increase of current with time of application of voltage in the reverse direction would tend to make the slope larger than it should be, and second when the voltage maximum is non-uniform over the surface the true Schottky slope is only approached asymptotically as the field is increased, so that the experimental slope is always somewhat larger than the theoretical slope.

The units analyzed were chosen to be representative of the variations that can be obtained by changes in either heat treatment or source of copper. With certain exceptions the resultant variation in magnitude of the parameters in Table I seems to be very minor. The conductivity of the oxide as determined by the density of acceptors and donors does not vary much except for units F and D where it is 3 to 5 times higher. The values of the parameters N_I, F_0, and l, deduced from the capacity of the various units, are all much the same, except for the case of the air quenched unit E, in which the width of the space charge layer is exceptionally large, with a correspondingly low ion density and low field strength at the metal surface. This particular variation is entirely reasonable. The slower rate of cooling results in a smaller density of copper defects or acceptors, thus reducing the net ion density in the space charge layer. The quantity V_s is a measure of the total potential change from inside the oxide layer to just outside the metal surface. For units A to E, where in each case the oxide is grown on copper, one might expect V_s to be the same. Changes in ion density in the oxide should only change the depth l and the field F in such a way as to give in every case the same V_s. Since V_s does vary, it must be that either the various processes result in a varying difference between the work functions of the copper and oxide surfaces, or it may be that some phenomena such as surface states on the oxide are playing an important role and variations in the density of surface states are the cause of the variations in V_s. If the copper-cuprous oxide interface were uniform and V_s were constant for the different processes of manufacture, then the only variation would be the ion density in the space charge layer. This variation in ion density would result in different capacities and different fields F_0. The only variation in the current voltage characteristic would be due to the different values F_0. All the variations in the rectifier as a circuit element would be due and traceable to how the processing affected the ion density. The analysis indicates, however, that the copper-cuprous oxide interface is not uniform. It acts like a patchy surface, the potential maximum varying in magnitude over the surface. Assuming, for the sake of argument, that the temperature coefficient of the potential maximum is small, the major variations in the current voltage characteristic would be due to variations in value of the potential maximum for the patches having the lower potential maximum (V_m') and the effective area (α) of these patches. It can be seen from the last section of Table I under I_m that both these parameters depend on the method of processing the rectifier, and one really has no clue as to why this should be so.

While this paper was being prepared, two somewhat different interpretations of the copper oxide rectifier characteristic have been published.[20,21] Both of these papers are primarily concerned with explaining just the experimental relation between current and voltage at one temperature. Both invoke a chemical barrier, i.e., a layer different from the rest of the oxide. On the other hand, the present paper suggests that when one analyzes all of the data on a single unit (capacity, conductivity of the oxide, current voltage characteristic, and temperature dependence) it is not necessary to assume such a special layer. It is, of course, very difficult to prove that any given explanation is necessary as well as sufficient. The present analysis does have internal consistency in that the important parameters determined in different ways do agree as to order of magnitude, and the additional assumption of a non-uniform interface is suggested by the nature of data and is certainly a reasonable one.

The author is indebted to J. Bardeen, whose help with the various theoretical aspects made this analysis possible. Most of the experimental work was done under the direction of J. A. Becker. Some of the more recent capacity data were taken by H. R. Moore.

[20] H. Y. Fan, Phys. Rev. **74**, 1505 (1948).
[21] F. Rose and E. Spenke, Z. Physik **126**, 632 (1949).