

## Electrical Conductivity of Single-Crystal Cuprous Oxide at High Temperatures\*

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The electrical conductivity of single-crystal  $\text{Cu}_2\text{O}$  was measured in the temperature range of  $1100^\circ$  to  $500^\circ\text{C}$  in oxygen pressures from 152 mm to  $10^{-5}$  mm of Hg. The  $\log\sigma$  vs  $\log P(\text{O}_2)$  curves were found to be linear between the oxygen pressures of 50 mm and  $10^{-2}$  mm, with an average slope of 0.1420, or approximately  $1/7$ . These curves exhibit a radical change in slope at  $\text{O}_2$  pressures below  $10^{-2}$  mm.

The plots of  $\log\sigma$  vs  $1/T$  at constant oxygen pressure were found to be linear and the activation energies obtained from the slopes of these plots have an average value of 0.65 ev at  $\text{O}_2$  pressures between 50 mm and  $10^{-2}$  mm. At  $\text{O}_2$  pressures of  $10^{-3}$  mm to  $10^{-4}$  mm, the activation energy increases sharply to a value of 1.05 ev. The activation energy obtained from the measurement of single-crystal  $\text{Cu}_2\text{O}$  in air at temperatures from  $1020^\circ\text{C}$  to  $1100^\circ\text{C}$  was found to have an average value of 0.767 ev.

An explanation for the physical significance of the activation energies obtained is suggested and the models proposed to explain the dependence of the electrical conductivity on the  $\text{O}_2$  pressure are considered.

### INTRODUCTION

THE semiconducting properties of  $\text{Cu}_2\text{O}$  have been of interest to investigators for many years, and as a result several excellent reviews on this material have appeared.<sup>1-3</sup> However, the majority of the data has been obtained on polycrystalline material and very little work has been done on single-crystal  $\text{Cu}_2\text{O}$  because a good method for producing large single crystals of  $\text{Cu}_2\text{O}$  was not available.

Thus the various reported measurements of the high-temperature conductivity have been performed on polycrystalline  $\text{Cu}_2\text{O}$ , with considerable variation in the resulting data. Some of the variation may be attributed to differences in the Cu from which the  $\text{Cu}_2\text{O}$  was prepared. However, the major fault probably lay with the preparation of the test sample. Previously, test samples were usually prepared by embedding Pt wire in a Cu specimen and then completely oxidizing the Cu to form the  $\text{Cu}_2\text{O}$  sample. An immediate fault in this method is that a sample prepared by the complete oxidation of a Cu sheet on all its free surfaces is not homogeneous, i.e., small voids form in the center of a plate or rod as a result of the complete oxidation of the Cu.<sup>4</sup> Also, during subsequent measurements at high temperatures grain growth can occur in the sample, and consequently the grain size cannot be controlled or specified. The effect of grain size on the conductivity at room temperature was investigated by Andrievskii,

Voloshchenko, and Mishchenko,<sup>5</sup> who found that the conductivity was directly proportional to the number of grains in the sample. If this effect is important at high temperatures, it would be impossible to maintain constant conditions in a polycrystalline sample unless it could be assured that the grain size remains constant.

The purpose of this paper is to present experimental data on the electrical conductivity  $\sigma$  of homogeneous single-crystal  $\text{Cu}_2\text{O}$  taken at temperatures between  $1100^\circ$  and  $500^\circ\text{C}$ , at  $\text{O}_2$  pressures from 152 mm to  $10^{-5}$  mm of Hg. Data are presented to show the variation of  $\sigma$  with  $\text{O}_2$  pressure at constant temperature, and the variation of  $\sigma$  with  $T$  at constant  $P(\text{O}_2)$ . The data are used to discuss the band structure of  $\text{Cu}_2\text{O}$  and to consider the validity of the models proposed to explain the dependence of  $\sigma$  on  $P(\text{O}_2)$ .

### II. EXPERIMENTAL METHOD

#### A. Sample Construction and Electrical Contacts

The samples used for measurement were obtained from large-area single-crystal plates of  $\text{Cu}_2\text{O}$  prepared by a selective annealing process described in a previous article.<sup>4</sup> Johnson-Matthey Cu sheet of purity 99.999+% was used as the starting material.  $\text{Cu}_2\text{O}$  plates were selected which contained grains each large enough to extract one or more rectangles of dimensions  $\frac{3}{4}$  in.  $\times$   $\frac{3}{8}$  in. The rectangles were cut from the single crystal by use of a diamond saw and 4 holes were drilled along one long edge for later application of contacts. The sample was given a light abrasive polish on one face and then was turned over and polished until the interface region containing the voids at the center of the plate was eliminated. This produced a uniform sample with a thickness of 0.020 in. to 0.015 in. depending on the original thickness of the  $\text{Cu}_2\text{O}$  plate. The sample was cut out using a dental sandblasting unit in design which allowed for two current and two voltage contacts. The sample was given a strong etch in dilute  $\text{HNO}_3$  and then

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<sup>1</sup> H. K. Henisch, *Rectifying Semiconductor Contacts* (Oxford University Press, London, 1957), pp. 88-94.

<sup>2</sup> G. F. J. Garlick, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. XIX, p. 377-380.

<sup>3</sup> J. S. Anderson and N. N. Greenwood, Proc. Roy. Soc. (London) **A215**, 353 (1952).

<sup>4</sup> R. S. Toth, R. Kilkson, and D. Trivich, J. Appl. Phys. **31**, 1117 (1960).

<sup>5</sup> A. I. Andrievskii, V. I. Voloshchenko, and M. T. Mishchenko, Doklady Akad. Nauk S.S.S.R. **90**, 521 (1953).

in an ammonium persulfate solution or a sodium cyanide solution.

Making electrical contact to  $\text{Cu}_2\text{O}$  is complicated by the fact that  $\text{Cu}_2\text{O}$  readily attacks most materials at high temperatures. Platinum has been found to be a material not readily attacked, and consequently was used for the contacts. To insure a good contact between the Pt and the  $\text{Cu}_2\text{O}$  already formed, small Cu hooks were inserted in the holes in the drilled sample and attached to the Pt contact wires. When the sample was heated to a high temperature, the Cu hooks became oxidized and formed a good  $\text{Cu}_2\text{O}$ - $\text{Cu}_2\text{O}$  contact and at the same time formed a good  $\text{Cu}_2\text{O}$ -Pt contact. Observations on the samples tested showed that the Cu hooks were completely oxidized.

### B. Furnace Assembly and Gas Regulation

The experimental apparatus used is shown schematically in the diagram of Fig. 1. The sample was suspended in the apparatus from a ground glass joint to which were attached two double-bore Alundum thermocouple tubes. Platinum wires were threaded through the tubes and attached to the sample as described above. An Alundum spacer was used to protect the sample from touching the wall of the furnace tube, which was either of quartz or Mullite. The sample temperature was read with a Pt-13% Pt-Rh thermocouple placed a few millimeters from the sample inside the tube. The gas flow into the system was regulated by a needle valve on the inlet side and by a constriction on the pump line, and was measured on a flow meter. In this manner, the sample was constantly bathed in the atmosphere passed into the furnace tube. Pressures as low as  $3 \times 10^{-5}$  mm were obtained by using a CEC GF-20A oil diffusion pump in conjunction with a Cenco Hyvac fore pump. The pressures were read on either a manometer, a 3-scale CEC Type GM-100 McLeod Gauge, or an ionization gauge.

The gases used in the experiments were pure  $\text{O}_2$ , air, or a special mixture of 0.001%  $\text{O}_2$  in  $\text{N}_2$  obtained from the Matheson Company. When air was used, the partial pressure of  $\text{O}_2$  was assumed to be 20%.

### C. The Measurement Circuit

The resistance of the samples was measured with a standard potentiometer circuit containing a Leeds and Northrup K-2 potentiometer and a Leeds and Northrup Type E galvanometer with a sensitivity of  $0.005 \mu\text{a}/\text{mm}$ .

### D. Experimental Procedure

The measurements on the samples were carried out over a wide range of  $\text{O}_2$  pressures and temperatures chosen so that only  $\text{Cu}_2\text{O}$  was the stable phase. The stability diagram shown in Fig. 2 was consulted to choose the range of temperatures and  $\text{O}_2$  pressures. In

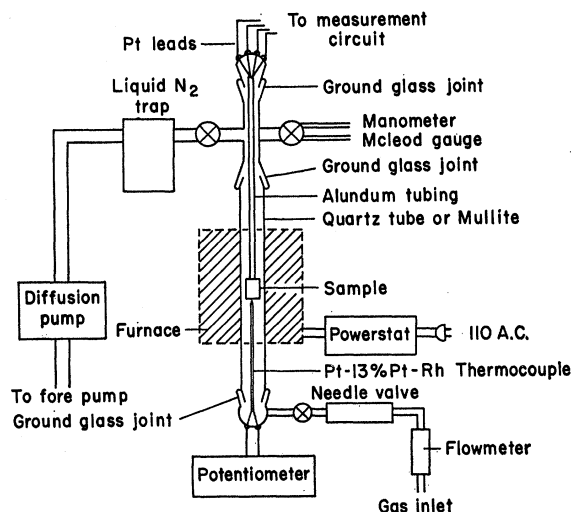


Fig. 1. Schematic drawing of the furnace assembly and gas regulation system used in the measurement of the high-temperature conductivity of  $\text{Cu}_2\text{O}$ .

each run the sample was brought to a high temperature by first placing it in the cold furnace tube and evacuating the tube to a pressure of  $10^{-3}$  mm. The temperature of the sample was increased rapidly to  $800^\circ\text{C}$  at this pressure. Pure  $\text{O}_2$  was then allowed into the furnace, and the  $\text{O}_2$  pressure and temperature were continuously adjusted within the  $\text{Cu}_2\text{O}$  stability region to reach a value of about 50 mm and  $1000^\circ\text{C}$  respectively. The samples were annealed under these conditions for at least one hour to insure that the Cu hooks were completely oxidized.

The measurements were initiated at this point, and all subsequent measurements were carried out at a constant  $\text{O}_2$  pressure. Thus, at the chosen  $\text{O}_2$  pressure the stability diagram was consulted to find the temperature region in which  $\text{Cu}_2\text{O}$  is stable. The high and low values of the temperature range for a given  $\text{O}_2$  pressure were chosen so that they were within the regions indicated

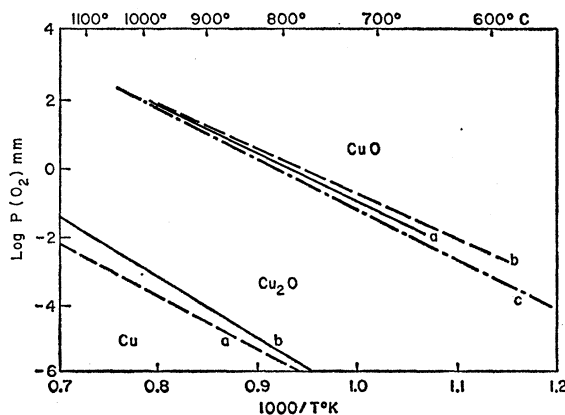


Fig. 2. Temperature dependence of the oxygen equilibrium pressure in the system  $\text{Cu}/\text{Cu}_2\text{O}/\text{CuO}$ ; (a) Gundermann, Hauffe, and Wagner,<sup>14</sup> (b) quoted by E. Engelhard, *Ann. Physik* 17, 501 (1933), and (c) after Hauffe, as quoted by Böttger.<sup>10</sup>

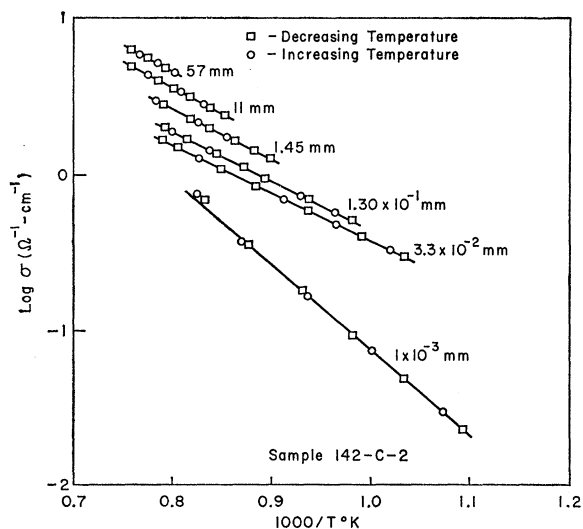


FIG. 3. Conductivity of  $\text{Cu}_2\text{O}$  as a function of temperature with the oxygen pressure as a parameter. Sample 142-C-2.

by the most conservative curves in Fig. 2. In all cases, the temperature was raised to the high value of the range and the sample was annealed at this condition for times ranging from 1 hour to 15 hours depending upon the  $\text{O}_2$  pressure, before the measurements were started. In this way complete equilibrium between the sample and atmosphere was assured before the measurements were taken.

Readings on the samples were taken over a complete cycle of the temperature range for a given  $\text{O}_2$  pressure starting from the high-temperature end, proceeding toward the low end, and then back to the high temperature. At  $\text{O}_2$  pressures of 150 mm to 1 mm, readings were taken every 10–20°C while at lower pressures temperature intervals of 25°–50°C were used. Fifteen- to twenty-minute intervals were allowed between individual measurements of the resistance and a check on the temperature immediately before and after each measurement showed a temperature variation of only  $\pm 1^\circ\text{C}$ .

The measurements were taken for both directions of the current and the average computed. The current was limited to less than 1 ma and was allowed to flow only when the measurements were in progress.

### III. EXPERIMENTAL RESULTS

#### A. Conductivity vs Temperature

Measurements were made on a total of 9 samples, and a typical set of results for the pressure range of 60 to  $10^{-3}$  mm is shown in Fig. 3. Figures 4 and 5 show the results for samples which were measured at lower pressures. The results of measurements for the pressure range 60 mm to  $10^{-4}$  mm were similar for all samples, and it can be seen from the agreement between points taken at decreasing and increasing temperature that no hysteresis effects occurred. This indicated that equi-

TABLE I. Average values for the conductivity (in  $\text{ohm}^{-1} \text{cm}^{-1}$ ) of single-crystal  $\text{Cu}_2\text{O}$  at different oxygen pressures with temperature as a parameter.

Pressure (mm Hg)	1000°C	950°C	900°C	850°C
50	4.82			
10	3.81	2.99	2.30	
1	2.77	2.16	1.67	1.25
0.1	1.99	1.56	1.22	0.90
0.01	1.42	1.12	0.88	0.66

brium existed between the sample and the atmosphere.<sup>6</sup> Average values for the conductivity at different  $\text{O}_2$  pressures and temperatures in this range are given in Table I. At pressures below  $10^{-4}$  mm, it was found that the measurements taken in the direction of increasing temperature did not reproduce those taken in the direction of decreasing temperatures. However, the plots for the decreasing temperature sequence were found to be still linear and these are shown in Figs. 4 and 5, with the caution that they may not represent equilibrium conditions. It is important to note that the values of the conductivity show an increase at  $10^{-5}$  mm and lower, over the value at  $10^{-4}$  mm.

There is some additional concern over the validity of the curves at pressures lower than  $10^{-4}$  mm due to the Knudsen effect. Since the sample is at a high temperature while the ionization gauge reading the pressure is at room temperature, a correction for the  $\text{O}_2$  pressure should be made for each experimental point. However, the points shown were plotted without applying the Knudsen correction since it was felt that the variation in the conductivity due to the changing temperature far outweighed any change due to the changing  $\text{O}_2$  pressure caused by the changing temperature. In any case it is

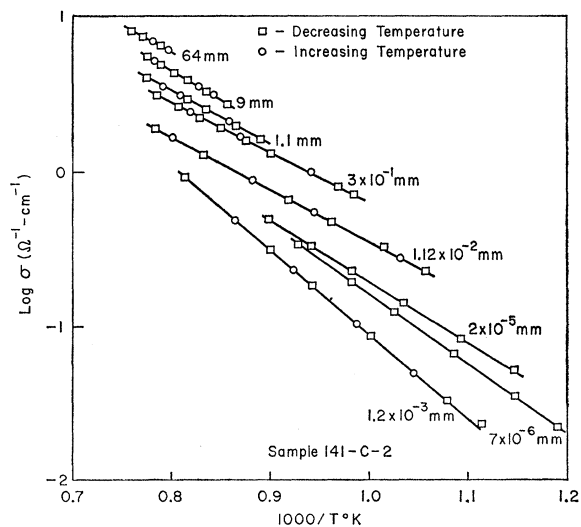


FIG. 4. Conductivity of  $\text{Cu}_2\text{O}$  as a function of temperature with the oxygen pressure as a parameter. Sample 141-C-2.

<sup>6</sup> G. Blankenburg, Ann. Physik 14, 290 (1954).

TABLE II. A comparison of average values for the conductivity (in  $\text{ohm}^{-1} \text{cm}^{-1}$ ) of  $\text{Cu}_2\text{O}$  at the oxygen pressure 152 mm Hg at different temperatures.

Temperature	1020°C	1050°C	1100°C
Our data	5.99	7.04	9.00
After Zuev	10.0	15.8	31.6

clear that the conditions and the existence of equilibrium in these samples cannot be as well specified as in the case of the equilibrium which did exist for  $\text{O}_2$  pressures about  $10^{-4}$  mm and above.

### B. Conductivity Measurements in Air

The conductivity of five samples was measured in air [ $P(\text{O}_2) = 152 \text{ mm}$ ] at high temperatures. Blankenburg and Kassel<sup>7</sup> and recently Zuev<sup>8</sup> have indicated that  $\text{Cu}_2\text{O}$  is stable in air at temperatures above 1020°C. Consequently, the measurements were carried out from 1020°C to 1100°C. The samples were annealed for two hours at a temperature of 1020°C or slightly higher to insure equilibrium. Measurements were made every 10°–15°C going up in temperature and again for decreasing temperatures. A typical curve, shown in Fig. 6, again exhibits no hysteresis. Average values of the conductivity for various temperatures in air are given in Table II.

### C. Activation Energies

The experimental curves of  $\log \sigma$  vs  $1/T$  are linear ( $\log \equiv \log_{10}$ ) and the data can be represented by the expression:

$$\sigma = \sigma_0 e^{-\epsilon/kT}. \quad (1)$$

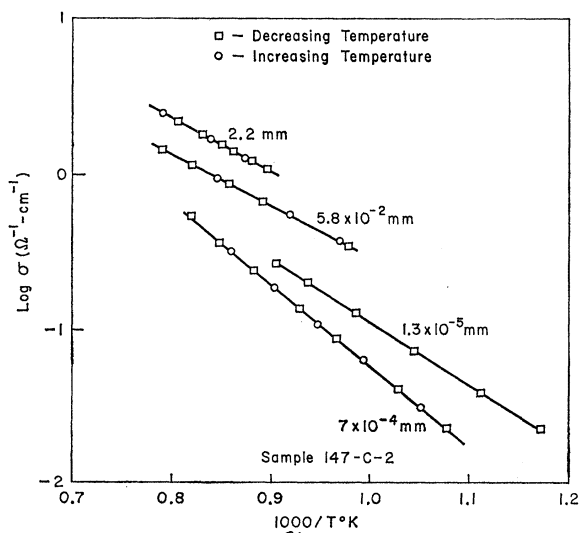


FIG. 5. Conductivity of  $\text{Cu}_2\text{O}$  as a function of temperature with the oxygen pressure as a parameter. Sample 147-C-2.

<sup>7</sup> G. Blankenburg and K. Kassel, *Ann. Physik* **10**, 201 (1952).

<sup>8</sup> K. P. Zuev, *Soviet Phys.-Solid State* **1**, 111 (1959).

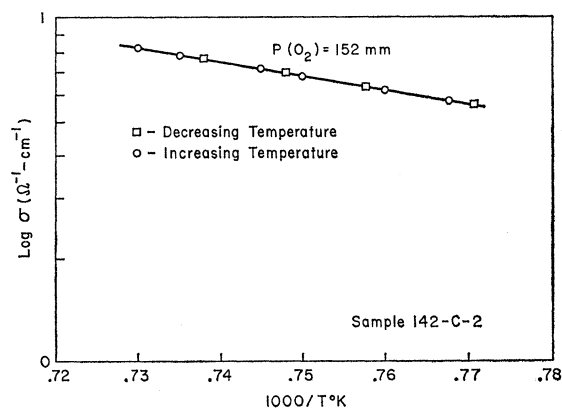


FIG. 6. Conductivity of  $\text{Cu}_2\text{O}$  in air as a function of temperature.

Consequently,  $\epsilon$ , the “activation energy” can be obtained from the slopes of the curves. Figure 7 shows the activation energies obtained as a function of the  $\text{O}_2$  pressure for all the samples tested. Points at pressures lower than  $10^{-3}$  mm are plotted without correcting for the Knudsen effect. As can be seen, the activation energy has an average value of 0.65 ev at  $\text{O}_2$  pressures from  $10^{-2}$  to 10 mm. At pressures of  $10^{-3}$  and  $10^{-4}$  mm, there is a sharp increase to a value near 1.05 ev. At  $\text{O}_2$  pressures above 100 mm, the curve begins to increase, and at 152 mm  $\epsilon$  has an average value of 0.767 ev.

### D. Conductivity vs Partial Pressure of Oxygen

From a comparison of the  $\log \sigma$  vs  $1/T$  curves it is seen that the conductivity varies with the  $\text{O}_2$  pressure. Thus the expression

$$\sigma \propto [P(\text{O}_2)]^x, \quad (2)$$

can be written, and from a plot of  $\log \sigma$  vs  $\log P(\text{O}_2)$  at constant temperature, the value of the exponent can be determined. Such a representation for the sample of Fig. 4 is given in Fig. 8. The points for the curves were obtained from the  $\log \sigma$  vs  $1/T$  curve by determining the conductivity at constant temperature at the various  $\text{O}_2$  pressures. In Fig. 8, it can be seen that the curves are linear over the pressure range 60 mm to  $10^{-2}$  mm, but that there is a sharp drop at lower pressures. At  $\text{O}_2$  pressures below  $10^{-3}$  mm the curves show a departure

TABLE III. Experimental slopes of the  $\log \sigma$  vs  $\log P(\text{O}_2)$  plots for  $\text{Cu}_2\text{O}$  for various temperatures.

$\text{Cu}_2\text{O}$ sample No.	1000°C	950°C	900°C	850°C
147-C-2	0.1420	0.1425	0.1410	0.1430
147-C-1	0.1404	0.1430	0.1391	
141-C-2	0.1400	0.1439	0.1439	0.1440
141-C-1	0.1460	0.1435	0.1415	0.143
132-C-1	0.140	0.1412	0.138	0.1335
132-C-2	0.1397	0.1397	0.1393	
142-C-2	0.1452	0.1488	0.1440	
Average	0.1419	0.1432	0.1410	0.1408

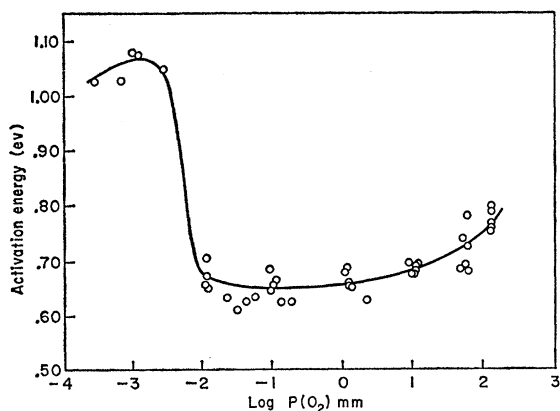


Fig. 7. Experimental activation energy for  $\text{Cu}_2\text{O}$  as a function of oxygen pressure at high temperatures.

from the linear behavior. Consequently the value of the exponent in Eq. (2) was obtained from the linear portion of the curves between the  $\text{O}_2$  pressures of 60 and  $10^{-2}$  mm. The values of the exponent for various temperatures are shown in Table III.

#### IV. DISCUSSION OF RESULTS

##### A. Numerical Value of the Conductivity

The experimental values of the conductivity determined here at the different temperatures and  $\text{O}_2$  pressures can be compared to the recent work by Stecker<sup>9</sup> and by Böttger<sup>10</sup> on polycrystalline  $\text{Cu}_2\text{O}$ . Table IV shows a typical comparison for data obtained at  $1000^\circ\text{C}$  for  $\text{O}_2$  pressures in the  $\text{Cu}_2\text{O}$  stability region. It can be seen that the variation among the results is not excessive considering the variation in specimen preparation and measurement technique. As mentioned previously, the existing variation in the values is thought to be due to the polycrystalline nature of the sample used by previous investigators, and to differences in the grades of Cu used to prepare the  $\text{Cu}_2\text{O}$  samples.

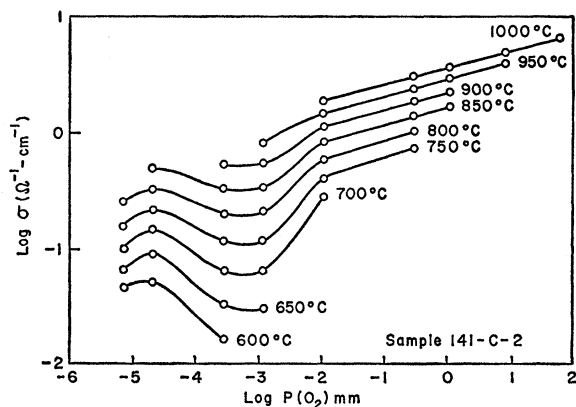


Fig. 8. Conductivity of  $\text{Cu}_2\text{O}$  as a function of oxygen pressure with temperature as a parameter.

<sup>9</sup> K. Stecker, *Ann. Physik* **3**, 55 (1959).

<sup>10</sup> O. Böttger, *Ann. Physik* **10**, 232 (1952).

TABLE IV. A comparison of values for the conductivity (in  $\text{ohm}^{-1}\text{cm}^{-1}$ ) of  $\text{Cu}_2\text{O}$  at  $1000^\circ\text{C}$  at different oxygen pressures.

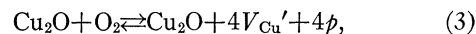
$\text{O}_2$ pressure	10 mm	1 mm	0.1 mm	0.01 mm
Our data	3.81	2.77	1.99	1.42
Böttger	0.50	0.36	0.25	0.20
Stecker	5.01	3.98	3.02	2.24

##### B. Conductivity of $\text{Cu}_2\text{O}$ in Air

The data obtained for  $\sigma$  in air can be compared with the results of Zuev,<sup>8</sup> who is the only previous worker to investigate this range. Using polycrystalline plates and sintered blocks, he obtained  $\log\sigma$  vs  $1/T$  curves which were linear from  $1020^\circ\text{C}$  to  $1070^\circ\text{C}$  but which increased in slope above  $1070^\circ\text{C}$ . Our results show a linear dependence of  $\log\sigma$  vs  $1/T$  from  $1020^\circ$  to  $1100^\circ\text{C}$  without any break at  $1070^\circ\text{C}$ . The average activation energy obtained from our data (0.767 eV), differs considerably from that obtained by Zuev in the  $1020^\circ$  to  $1070^\circ\text{C}$  region (0.95 to 1.00 eV). A considerable variation in the numerical values of  $\sigma$  exists between these two sets of data, as shown in Table II.

##### C. Dependence of $\sigma$ on $P(\text{O}_2)$

Since it is well known that  $\text{Cu}_2\text{O}$  prepared at high  $P(\text{O}_2)$  is a  $p$ -type semiconductor and it has been conclusively demonstrated that  $\sigma$  depends upon the ambient  $\text{O}_2$  pressure present in the preparation period, models have been proposed to explain this dependence assuming  $p$ -type conduction. Wagner and Hammen<sup>11</sup> were the first to postulate an equilibrium between the  $\text{O}_2$  and solid  $\text{Cu}_2\text{O}$  of the form



where  $V_{\text{Cu}}'$  represents a Cu ion vacancy and  $p$  represents an electron hole.<sup>12</sup> Applying the law of mass action, and defining an equilibrium constant,  $k_{\text{ox}}$ , for the reaction of Eq. (3), they obtained

$$p^4(V_{\text{Cu}}')^4 = k_{\text{ox}}P(\text{O}_2). \quad (4)$$

Assuming that at high temperatures the electrical neutrality condition was  $(V_{\text{Cu}}') = p$ , they obtained the relation  $p^8 = k_{\text{ox}}P(\text{O}_2)$ . They then assumed that the conductivity was due primarily to hole conduction and arrived at the relation

$$\sigma = K_{\text{ox}}[P(\text{O}_2)]^{1/8}. \quad (5)$$

However, the experimental work by Wagner and co-workers<sup>13,14</sup> showed that  $\sigma$  varies with  $P(\text{O}_2)$  to the  $1/7$

<sup>11</sup> C. Wagner and H. Hammen, *Z. physik. Chem.* **B40**, 197 (1938).

<sup>12</sup> We use here the notation of F. A. Kroger and H. J. Vink, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 3, Chap. 3, p. 307.

<sup>13</sup> H. Dunwald and C. Wagner, *Z. physik. Chem.* **B22**, 212 (1933).

<sup>14</sup> J. Gundermann, K. Hauffe, and C. Wagner, *Z. physik. Chem.* **B37**, 148 (1937).

TABLE V. Calculated concentrations of imperfections in  $\text{Cu}_2\text{O}$  at  $1000^\circ\text{C}$  (Based on a model suggested by Bloem).

$P(\text{O}_2)$ (mm Hg)	$\sigma$ (exptl) ( $\text{ohm}^{-1}\text{cm}^{-1}$ )	$k_{\text{ox}}P(\text{O}_2)$ ( $\text{cm}^{-24}$ )	$k_{\text{ox}}$ ( $\text{cm}^{-24})(\text{cm Hg})^{-1}$ )	$p$ ( $\text{cm}^{-3}$ )	$n$ ( $\text{cm}^{-3}$ )	$V_0'$ ( $\text{cm}^{-3}$ )	$V_0''$ ( $\text{cm}^{-3}$ )
50	4.82	$6.56 \times 10^{147}$	$1.31 \times 10^{147}$	$3 \times 10^{18}$	$1.67 \times 10^{16}$	$9.5 \times 10^{16}$	$1.14 \times 10^{14}$
10	3.81	$1.31 \times 10^{147}$		$2.45 \times 10^{18}$	$2.02 \times 10^{16}$	$1.74 \times 10^{17}$	$1.71 \times 10^{14}$
1	2.77	$1.31 \times 10^{146}$		$1.84 \times 10^{18}$	$2.72 \times 10^{16}$	$4.12 \times 10^{17}$	$3.0 \times 10^{14}$
0.1	1.99	$1.31 \times 10^{146}$		$1.38 \times 10^{18}$	$3.62 \times 10^{16}$	$9.73 \times 10^{17}$	$5.4 \times 10^{14}$
0.01	1.42	$1.31 \times 10^{144}$		$1.03 \times 10^{18}$	$4.85 \times 10^{16}$	$2.33 \times 10^{18}$	$9.8 \times 10^{14}$

power, in the  $P(\text{O}_2)$  range  $10^{-2}$  mm to 10 mm Hg. The recent experimental work by Böttger<sup>10</sup> has also shown the 1/7 power behavior in this pressure range. At lower  $P(\text{O}_2)$  he found  $\sigma$  to vary in an anomalous way with  $P(\text{O}_2)$  and to deviate considerably from the 1/7 relation. In comparison, Stecker<sup>9</sup> has found the dependence to be 1/8.3, more in line with the original Wagner theory. All of these previous measurements were performed on polycrystalline  $\text{Cu}_2\text{O}$ .

Our data obtained on single-crystal  $\text{Cu}_2\text{O}$  support the work of Wagner and Böttger and indicate this dependence of 1/7 to be a real value. Thus the deviation from the theoretical value of 1/8 is probably not simply due to errors in experimentation or sample preparation. Consequently the original simplified Wagner model must be modified to account for the experimental result. A recent attempt to do this has been made by Bloem,<sup>15</sup> who carried out a more detailed analysis assuming only Schottky-Wagner disorder in  $\text{Cu}_2\text{O}$ . His theory predicted the 1/7 behavior, and consequently we used our data to test his model. In order not to reproduce his entire treatment here, we will discuss only the essential features and give the final results.

Bloem's model assumes that there exist singly and doubly ionized anion vacancies in addition to the cation vacancies, and that association of defects may occur. A more general electrical neutrality condition is then written as

$$n + (V_{\text{Cu}}') = p + (V_0') + 2(V_0''), \quad (6)$$

where  $n$  is the density of electrons, and  $(V_0')$  and  $(V_0'')$  represent the concentrations of singly and doubly ionized anion vacancies, respectively. The concentrations of the carriers and defects depend upon the  $P(\text{O}_2)$ , and in certain  $P(\text{O}_2)$  ranges the neutrality condition [Eq. (6)] can be simplified to only two terms. Thus at high  $P(\text{O}_2)$  Bloem assumes Eq. (6) to reduce to  $p = V_{\text{Cu}}'$ . This corresponds to the original Wagner assumption and leads to the 1/8 relationship [Eq. (5)]. As  $P(\text{O}_2)$  becomes smaller, the concentrations of the defects change so that the neutrality condition in the next range is assumed to become  $(V_0') = (V_{\text{Cu}}')$ . By calculating  $\log \sigma$  vs  $\log P(\text{O}_2)$  at medium oxygen pressures, Bloem indicates that a slope of 1/7 is found.

Using the equilibrium constants arrived at by Bloem, we used our data to calculate the defect and carrier concentrations starting from the high  $\text{O}_2$  pressures to

lower pressures. These results are shown in Table V. As can be seen in the table, the concentration of  $V_0'$  becomes larger than the hole concentration  $p$  at  $P(\text{O}_2)$  between 0.1 and 0.01 mm Hg. Therefore, a change to the 2nd neutrality condition would be necessary here. However, this would change the slope of the  $\log \sigma$  vs  $\log P(\text{O}_2)$  curve only near the end portion. Thus, Bloem's model also predicts the 1/8 behavior in the region where the experimental data indicate the 1/7 power.

It is possible that the equilibrium constants are in error and need modification to achieve a satisfactory agreement with Bloem's model. This could be done without violating established data, since the effective masses and mobilities of both holes and electrons in  $\text{Cu}_2\text{O}$  have not been determined at high temperatures. It is also possible to introduce new reactions involving Frenkel-type defects together with the Schottky-Wagner defects to account for the 1/7 dependence.

However, it is felt that such arbitrary assumptions and evaluation of constants would not give a concrete foundation to a model which would explain the experimental results. It is felt that more useful information can be obtained by further experiments, in particular the evaluation of mobilities of the carriers at high temperatures, and the establishment of the existence of other types of defects.

#### D. Activation Energies

Many different values for the activation energy at high temperatures have been reported in the literature. This has been due primarily to the fact that the  $\text{O}_2$  pressure was not always controlled and specified in the experiments. Recent data, however, are in better agreement than earlier reported values. The results reported here in the  $\text{O}_2$  pressure range of  $10^{-2}$  mm to 10 mm agree favorably with the value obtained by Böttger<sup>10</sup> (0.62 eV) and Stecker<sup>9</sup> (0.65 eV) in the same pressure range. At pressures above 10 mm, we can compare our results only with those reported by Zuev. His reported value of 0.95–1.00 eV is considerably higher than our value of 0.767 eV at 152 mm. However it is significant to note that the activation energy in our data does show an appreciable increase at the high  $\text{O}_2$  pressure. At pressures below  $10^{-3}$  mm, our data show a sharp increase to 1.05 eV. This agrees favorably with an increase to 0.95 eV reported by Böttger in this region. Stecker, on the other hand, did not find this increase in his results.

<sup>15</sup> J. Bloem, Philips Res. Repts. **13**, 167 (1958).

The activation energy of 1.05 eV reported by Anderson and Greenwood<sup>8</sup> agrees very well with our value. They measured  $\sigma$  vs  $T$  from high to very low temperatures by continuously adjusting the  $O_2$  pressure to maintain  $Cu_2O$  stable but without specifying the values for  $P(O_2)$ . It is conceivable that their measurement of  $\sigma$  at high temperature was carried out at  $P(O_2)$  of  $10^{-3}$  mm, since this pressure allows a wide and convenient temperature range in which  $Cu_2O$  is stable.

The physical meaning of the activation energies experimentally obtained has not been clear. Several investigators<sup>2,15</sup> have assumed that the activation energy of 0.65 eV represents the energy required to lift an electron from the valence band to an impurity level 0.65 eV above it. However, low-temperature data show that the impurity level is 0.30 eV to 0.35 eV above the valence band. On the basis of this result, Feldman<sup>16</sup> postulated that the 0.65-eV value represents a combination of two processes, the electronic excitation energy and the heat of formation of the defect. Recently Rudolph<sup>17</sup> has postulated a similar interpretation for activation energies obtained on other compound semiconductors. Unfortunately, the value for the heat of formation for the cation vacancy in  $Cu_2O$  is not known and consequently it is not possible to isolate the electron excitation energy.

However, it is quite probable that the concentration of defects does not remain constant as the temperature is varied and that an energy change is associated with the creation of defects. Thus it is our opinion that the experimental activation energy of 0.65 eV does not represent an electronic excitation to an impurity level 0.65 eV above the valence band. In the simplest model, based on Wagner's original model, one could explain the experimental activation energy as being due to the energy required to create a neutral copper vacancy and the energy required to ionize this vacancy. Thus one could assign a value of about 0.3 to 0.4 eV to the ionization of the vacancy, based on low-temperature conductivity data, and assign the remainder of the 0.65 eV to the energy of formation of the vacancy. If a more complex model is chosen, such as Bloem's, the experimental activation energy would be a properly weighted com-

posite of several contributing temperature coefficients such as those involving the heat of formation of the neutral Cu and oxygen vacancies, the thermal ionization energies of the copper vacancy acceptors and the oxygen vacancy donors, and the thermal band gap.

It is seen that the activation energy increases at both the high and low ends of the curve in Fig. 7. In the high-pressure—high-temperature range, Zuev has postulated that the activation energy he obtained (0.95–1.0 eV) corresponds to intrinsic conduction in  $Cu_2O$ . He supports this statement by his observation that, at temperatures of 1050°C and higher, the  $Cu_2O$  becomes enriched with Cu, and from the fact that the band gap of  $Cu_2O$  has been found to be 2.176 eV.<sup>18</sup> Our value of 0.767 eV is somewhat smaller and certainly rules out the possibility of solely intrinsic conduction in this range. However, it does appear that the increase from 0.65 eV to 0.767 eV in our results at higher temperatures is due to the steadily increasing effect of intrinsic excitation.

The increase in activation energy at low  $O_2$  pressures is more abrupt than at high pressures. This sudden increase suggests a change in mechanism for the generation of carriers. Anderson and Greenwood proposed that their value of 1.05 eV for activation energy represented intrinsic conduction. This seems reasonable since  $Cu_2O$  should tend to become less  $p$  type as the  $O_2$  pressure decreases. It is our feeling that the sudden increase in activation energy and decrease in conductivity in our data in this pressure range is due to a change to intrinsic conduction. The subsequent decrease in activation energy and increase in  $\sigma$  as the  $O_2$  pressure becomes still smaller is thought to be due to the advent of  $n$ -type conduction. However, it must be pointed out again that the data at these low  $O_2$  pressures were obtained under conditions that may not have represented equilibrium.

The indication that  $Cu_2O$  becomes an intrinsic conductor at low  $O_2$  pressures and then tends toward  $n$ -type conduction as the  $O_2$  pressure is further decreased has been a point of controversy in the literature.<sup>1</sup> Work is now being carried out in our laboratories to measure the Hall effect at high temperatures in order to resolve this problem. Low-temperature measurements on single crystals of  $Cu_2O$  are also in progress.

<sup>16</sup> W. Feldman, Phys. Rev. 64, 113 (1943).

<sup>17</sup> J. Rudolph, Z. Naturforsch. 14a, 727 (1959).

<sup>18</sup> E. F. Gross and I. Pastrnyak, Soviet Phys.-Solid State 1, 758 (1959).