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The Electrical Conductivity and Isothermal Hall Effect in Cuprous Oxide

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The electrical conductivity of cuprous oxide is studied from room temperature to 700°C. It is observed that whereas the conductivity may be represented by the formula $\sigma = A e^{-\epsilon/kT}$ at the higher temperatures, below 300°C the exponential law is not obeyed. The maxima and minima of the conductivity curves observed in the latter region are presumed to result from a combination of a saturation of clusters and a rapid decrease of mobility with temperature. Hall effect measurements up to 450°C show that the number of current carriers does not obey the exponential law of temperature dependence. An anomaly in the mobility is observed around 150°C where the mobility changes from a T^{-5} to a T^{-7} dependence.

INTRODUCTION

THE semi-conductor, cuprous oxide, has been the object of many investigations in the past decade because of its peculiar electrical properties which are of theoretical and technical importance. However, the results and interpretations of these investigations have differed so markedly as to prevent the formulation of a unique theory of conduction in cuprous oxide. Englehard[1] and Angello[2] have studied the dependence of the conductivity and Hall coefficient on the impurity content and past history of various specimens. Their results indicate that the conductivity increases rapidly with rise in temperature and with an increase in the concentration of excess oxygen in the lattice. The Hall coefficient is positive, indicating that the current carriers are positively charged. Vogt[3] reached the same conclusion as a result of measurements of the thermoelectric effect. Between 100°C and 1000°C Jusé and Kourtschatow[4] and Dünwald and Wagner[5] have investigated the electrical conductivity. Jusé and Kourtschatow determined the excess oxygen content of their specimens at room temperature and attempted to correlate this with the conductivity. They concluded that at the high temperatures the electrical conductivity was an intrinsic property of the cuprous oxide and depended solely on the temperature. Dünwald and Wagner, on the other hand, investigating the effect of varying the external oxygen pressure on the specimen at constant temperature observed that the conductivity varied as the 1/7 power of the oxygen pressure. This indicates that the conductivity is a function of the amount of absorbed oxygen. The only data on the Hall effect at high temperatures are those of Schottky and Waibel,[6] who interpreted their data initially as indicating a change in the sign of the Hall coefficient. In a later paper Schottky concluded that this interpretation was erroneous. Thermoelectric measurements made at high temperatures by Dünwald and Wagner showed that the sign of the current carriers was positive.

The evidence of the above works indicates that cuprous oxide fits into the band theory of solids in the following manner: Pure cuprous oxide is an insulator which possesses a gap of at least one ev between the top of the highest filled band and the bottom of the lowest unfilled band. When cuprous oxide is in equilibrium with oxygen gas it absorbs oxygen so that the composition is no longer stoichiometric. The absorbed oxygen produces empty discrete energy levels which lie within the forbidden region but close to the top of the filled band. Thermal excitation of electrons to these levels results in electron "holes" in the lower band. The resulting conductivity is then apparently due to positively charged particles. In addition, it is strongly dependent upon the concentration of the ab-

[1] E. Englehard, Ann. d. Physik **17**, 501 (1933).
[2] S. J. Angello, Phys. Rev. **62**, 371 (1942).
[3] W. Vogt, Ann. d. Physik **7**, 183 (1930).
[4] W. Jusé and B. W. Kourtschatow, Physik. Zeits. Sowjetunion **2**, 453 (1932).
[5] H. Dünwald and C. Wagner, Zeits. f. physik. Chemie **22B**, 212 (1933).
[6] W. Schottky and F. Waibel, Physik. Zeits. **34**, 858 (1933); **36**, 912 (1935).

sorbed oxygen. At low temperatures (less than 300°C) the rate at which equilibrium is established between the absorbed oxygen in the solid phase and the gas phase is so low that it is impossible to control the concentration of absorbed oxygen by varying the pressure of the oxygen gas. Thus, the electrical properties at low temperatures depend upon the past history of the sample, such as the manner in which it was cooled from elevated temperatures. At high temperatures, where equilibrium may be assumed, the following mechanism is postulated for the absorption of the oxygen.[7] Oxygen molecules are absorbed on the surface of the cuprous oxide, and copper ions and electrons diffuse to the surface to form additional cuprous oxide with the oxygen molecules. This diffusion process leaves copper ion vacancies in the lattice. The process may be summarized by the reaction

$$2Cu^{+}+\tfrac{1}{2}O_2(\text{gas})\rightarrow 2Cu_h^{++}+O^{=}+2Cu^{+},$$

where Cu_h^{++} represents a copper ion vacancy in the lattice with an electron "hole" bound to a neighboring Cu^{+} ion. This copper ion vacancy is the source of a discrete energy level which lies in the forbidden region. By minimizing the free energy of the above system one obtains the relation for the number of copper ion vacancies

$$n_b=N_0T^{-5/8}p^{\frac{1}{4}}\exp(-W/kT),$$

where n_b is the number of copper ion vacancies, p is the pressure of the oxygen gas, $2W$ is the energy needed to place an oxygen atom in the lattice and produce two copper ion vacancies, N_0 is a constant, and k is Boltzmann's constant. It is assumed that n_b is small compared with the number of particles in the solid and also in the surrounding gas.

Using this expression for n_b we may now determine the number of free electron holes to be expected at a given temperature. It is assumed that the ionization of a hole may be treated as if equivalent to the reaction

$$Cu_h^{++}\rightleftarrows Cu_h^{+}+h.$$

Minimizing the free energy of the reaction with respect to a change in the number of free holes, h, we obtain

$$h=h_0n_b^{\frac{1}{2}}T^{\frac{3}{4}}\exp(-E/kT),$$

where E is the energy necessary to free a hole. Using the expression for n_b we have

$$h=\text{const. }p^{1/8}T^{7/16}\exp(-\epsilon/kT),$$

where $\epsilon=W+E$.

With the assumption that the free electron holes may be treated as a perfect gas, their contribution to the electrical conductivity may be calculated by simple classical theory.[8] The conductivity under these conditions is given by $\sigma=ne\mu$, where n is the number of free holes per unit volume, e is the charge of a hole, and μ the mobility of the carriers obtained from the relation $\mu=4el_0/3(2\pi m^*kT)^{\frac{1}{2}}$, where l_0 is the average mean free path and m^* the effective mass of the holes. Using the equation above for the number of free holes we obtain for the conductivity

$$\sigma=\text{const. }p^{1/8}T^{-1/16}l_0\exp(-\epsilon/2kT).$$

This equation can be expected to be valid only when the temperature is sufficiently high so that equilibrium conditions are established at all times. At low temperatures when equilibrium is not established the number of oxygen atoms absorbed will be independent of the temperature and one would expect the conductivity to show an exponential dependence on temperature with an activation energy E. Of course, the assumption is made that the copper ion vacancies in the lattice do not interact with each other. If, however, the density of copper ion vacancies is large enough for this to happen, one might expect a decrease in the activation energy.[9] In the preceding discussion it has been assumed that the mean free path is either constant or is a slowly varying function of the temperature and impurity content. This should be true at the higher temperatures, since the theory assumes that the mean free path is determined by the interaction of electrons with lattice vibrations.

In any case, a measurement of the Hall coefficient in conjunction with conductivity measurements allows one to determine both the

[7] C. Wagner, Trans. Faraday Soc. **34**, 851 (1938).

[8] F. Seitz, *Modern Theory of Solids* (McGraw-Hill, New York, 1940), p. 190.

[9] P. H. Miller, Jr., Phys. Rev. **60**, 890 (1941).

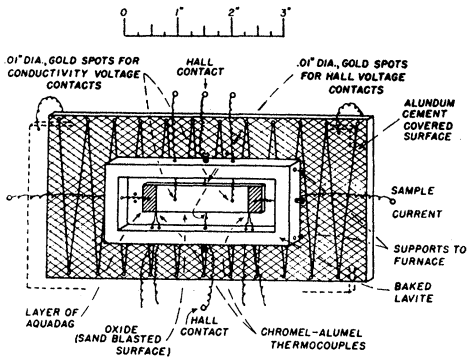

FIG. 1. Schematic diagram of furnace, specimen holder, and specimen in position for measurements.

number of carriers and the mobility independently. The Hall coefficient R is given by the relation $R=-3\pi/8nec$ and the product of the Hall constant and the conductivity gives the mobility

$$\mu=-8R\sigma/3\pi c.$$

If one compares the simple theory with the results of the investigations on cuprous oxide the following conclusions are reached: At high temperatures the conductivity can be expressed rather well by an equation of the form

$$\sigma=\sigma_0 \exp(-U/kT),$$

where U is apparently the same for all samples. Therefore, Jusé and Kourtschatow[4] conclude that this high temperature conductivity is intrinsic. On the other hand, the results of Dünwald and Wagner[5] indicate that the conductivity depends upon the excess oxygen concentration. Furthermore, the work of Waibel and Schottky[6] on the Hall effect at high temperatures indicates that the number of current carriers is not a simple exponential function of the temperature, and that the mobility is a very rapidly varying function of the temperature.

EXPERIMENTAL PROCEDURE

The specimen holder as shown in Fig. 1 is a lavite block which is milled to accommodate the specimen. The Hall and conductivity contacts, as indicated, are made of Nichrome wire which offers the advantage of being able to retain its spring at the higher temperatures. Enclosing the specimen holder is a rectangular transite furnace in which are embedded Nichrome heating elements. These are covered with a mixture of Alundum cement and sodium silicate. Narrow strips of transite separate the two furnace walls and the entire unit is clamped together with screws.

The furnace and holder are mounted between the pole faces of an electromagnet which is made of two cylinders of Armco iron. With 12 amperes through the windings and an air gap of $\frac{3}{4}''$ the field is 7150 gauss at room temperature, as calibrated with a bismuth spiral. All electrical measurements are made with a Leeds and Northrup type K potentiometer. The temperature of the furnace was controlled manually, and temperature measurements of the specimen were made with two Chromel-Alumel thermocouples placed at opposite ends of the sample.

The cuprous oxide was prepared from strips of Chilean copper, $2\frac{1}{4}''\times\frac{1}{2}''\times\frac{1}{16}''$ which were suspended in a furnace at 1000°C for 16 hours.[10] This time was sufficient to effect a complete oxidation of the specimen. After oxidation the sample was placed in an annealing furnace for two hours at a predetermined temperature and then quenched in cold tap water.

Gold contacts, about 0.01″ in diameter, evaporated on the specimen, were used for most measurements although it was observed that aluminum gold combinations responded as well. A schematic diagram of the specimen is given in Fig. 1 which also indicates the position of the probes for measurements.

For the Hall measurements two B batteries were used to supply the sample current. It was found advisable to keep the current below one milliampere while fresh samples were being used, since the use of larger currents caused aging,[2] or a decrease in the number of carriers. The e.m.f.'s which are determined initially with the potentiometer must be corrected for the contribution due to electrode misalignment and temperature gradients. Both of these effects are eliminated by taking two readings, one with the magnetic field in a fixed direction, and the other with the field reversed. From the theory of the

[10] The samples of cuprous oxide were kindly furnished by Mr. C. C. Hein of the Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania. A typical analysis of the copper and also the processing technique are given in reference 2.

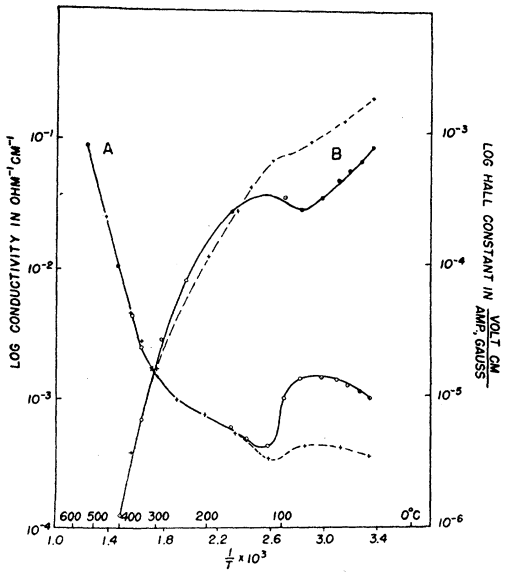

FIG. 2. Conductivity (curve *A*) and Hall constant (curve *B*) as a function of temperature for a fresh sample of CuO_2 quenched from 450°C.

Hall effect the Hall coefficient is given by the equation

$$R = E_H d/IH,$$

where d is the thickness of the specimen, H is the magnetic field in gauss, and I is the specimen current in amperes.

Immediately following the Hall measurements point-probe conductivity determinations are made. The method consists of measuring the potential drop across a fixed portion of the specimen while a known current is flowing in the specimen. The advantage of the technique is that no current is drawn by the probes. The potential drop measured across the probes must be corrected for the contribution due to the thermal e.m.f. Around 100°C the latter represents about a 2 percent correction, and continues to increase till at 900°C the thermal e.m.f. becomes comparable with the true potential drop across the probes. This, of course, depends upon the current flowing through the specimen. For currents of 10 milliamperes the correction at the higher temperatures is about 8 percent, while for one milliampere it approaches 20 percent.

RESULTS AND INTERPRETATION

In Fig. 2 are shown two curves (*A*) giving the variation with temperature of the logarithm of the specific conductivity for a specimen of cuprous oxide quenched from 450°C. The upper curve was obtained with rising temperature and the lower curve with decreasing temperature. The various points were taken at time intervals of twenty minutes. It may be noted that on the lower curve corresponding values of the conductivity at a given temperature have decreased considerably. This is indicative of a definite aging process in which an appreciable number of the current carriers is depleted. Attempts were made to obtain a reversible curve for a fresh sample by making the measurements rapidly. However, the rapidity with which aging set in above 60°C made this impossible. Also, the temperature to which the sample was raised during the run, and the speed of cooling may have influenced the amount of absorbed oxygen and removed all significance from the results.

In curves (*B*) of Fig. 2 are given the Hall constant curves for the same specimen. These curves bear a one to one correspondence relative to the conductivity curves. The regions at which the conductivity shows a hump are those at which the Hall coefficient has a plateau, and the regions at which the conductivity rises rapidly the Hall coefficient decreases rapidly. It might be remarked that the curves of Fig. 2 are representative of the initial behavior of specimens that were quenched from different temperatures. The only distinction is in the magnitude of the Hall constant and the specific conductivity. Since the Hall constant decreases and the conductivity increases with an increase in the number of carriers, we should expect that at a given temperature the latter will be large if the former is small, and vice versa.

In Fig. 3 (curve *A*) are given the conductivity curves for a well-aged specimen run in air. The specimen had previously been quenched from 250°C. The curves exhibit the same sort of characteristics as those in Fig. 2; however, we shall consider them in more detail. At the higher temperatures the conductivity increases in a manner described by a Boltzmann relationship, but below 300°C a marked deviation occurs. Part of the deviation can be explained by assuming that true equilibrium is not attained at the lower temperatures, that is, that oxygen is

frozen in the lattice. It was possible to quench a given sample with a blast of cold air from a given temperature to room temperature and obtain conductivities which varied by a factor of 20. The higher the quench temperature the higher was the room temperature conductivity. This feature accounts for the many branches in the low-temperature region of the curve. These differences in the conductivity disappear around 300°C for above this temperature all curves follow the same pattern. Presumably, the rate of diffusion of oxygen is sufficiently large in the neighborhood of 300°C to bring about equilibrium in the time allotted between measurements. The slope of the curves in the high temperature region turns out to be 0.78 ev and remains the same for all specimens regardless of past history. This slope agrees quite well with that obtained by Jusé and Kourtschatow[4] who found an activation energy for the high temperature part of their curves of 0.72 ev.

An experiment similar to that of Dünwald and Wagner[5] was performed in order to test for the pressure dependence of the resistance of cuprous oxide. A small slab of cuprous oxide was placed between two platinum contacts which were forced together by a spring, and the specimen was then placed in a furnace at 850°C. Resistance measurements were made for various oxygen pressures, and the resistance was found to vary markedly in the range of 10^{-2} to 150 mm oxygen pressure. In Fig. 4 is shown the variation of the logarithm of the resistance with the logarithm of the oxygen pressure for two specimens. The results of several samples give slopes ranging from 1/6.8 to 1/7.2 which agree quite well with Wagner's value of 1/7. However, the departure from a 1/8 law as evidenced in all specimens appears to be a real property of cuprous oxide. Wagner suggests that an incomplete dissociation of the ions and electrons might be the cause of the disagreement.

Figure 3 (curves B) show the variation of the Hall constant with temperature for a well-aged sample. The surprising result obtained from these curves is that n, the number of carriers, cannot be represented by the relation

$$n = n_0 \exp(-\epsilon/kT),$$

where n_0 and ϵ are constant. Data taken from the curves show that ϵ varies from about 1.0 ev at 450°C to about 0.1 ev at room temperature. This agrees qualitatively with the Hall effect data of Waibel and Schottky;[6] however, no evidence was found for a change in sign of the Hall coefficient.

Figure 5 shows the behavior of the mobility as a function of temperature. Again, qualitative agreement is obtained with the data of Waibel and Schottky. The mobility varies approximately as T^{-5} from room temperature to 150°C, and it varies approximately as T^{-7} from 150°C to 450°C. This means that the conductivity, alone, cannot give accurate information concerning the variation of the number of carriers with temperature. Furthermore, it seems difficult to explain this rapid variation of the mobility by assuming that the electrons are scattered only by lattice vibrations. One wonders whether some scattering or trapping process involving the number of impurity centers is not responsible for the observed behavior. It is difficult to reach any definite conclusions at present because little is known about the interaction of slow electrons with lattice vibrations.

In conclusion the results may be summarized as follows:

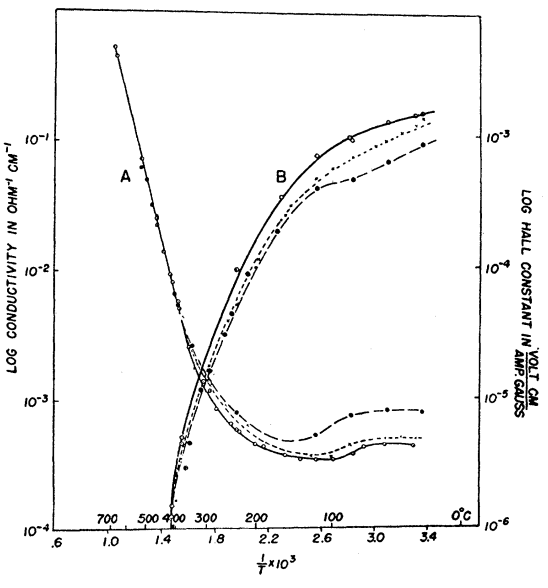

FIG. 3. Conductivity (curves A) and variation of the Hall constant (curves B) of a well-aged sample of cuprous oxide as a function of temperature. The slope of the curve A at the higher temperatures is 0.78 ev.

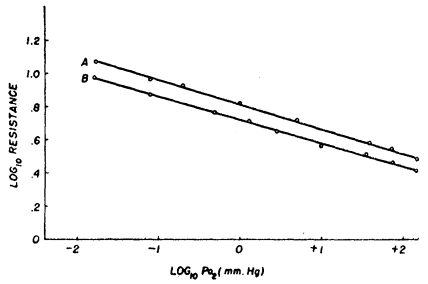

FIG. 4. Resistance as a function of oxygen pressure for two specimens of cuprous oxide measured at 850°C. Slope of curve A is 1/6.8; curve B, 1/7.1.

(1) There is no evidence that an intrinsic conductivity exists in cuprous oxide.

(2) There is no evidence for a change in sign of the Hall coefficient.

(3) The simple theory of semi-conduction needs considerable extension before it can fully explain the data. However, the following general interpretation is suggested. At low temperatures a frozen equilibrium exists in cuprous oxide, and the number of absorbed oxygen atoms is independent of the temperature. The extremely low activation energy observed in this range of temperature is to be associated with the formation of clusters of centers, in the sense suggested by Miller[9] for the case of zinc oxide. The maxima and minima of the conductivity curves observed in the low temperature region result from a combination of a saturation of the clusters and the rapid decrease of the mobility with temperature. Above 300°C an equilibrium exists between the absorbed oxygen and the external oxygen gas. As a result, the number of oxygen atoms absorbed and the fraction of holes ionized depend exponentially upon the temperature. Apparently, we must believe that one or both of the activation energies, E and W (E is the energy to free an electron hole and W is the energy to place an oxygen atom in the lattice as an ion and produce two copper ion vacancies), are functions of the temperature, or the concentration of absorbed oxygen.

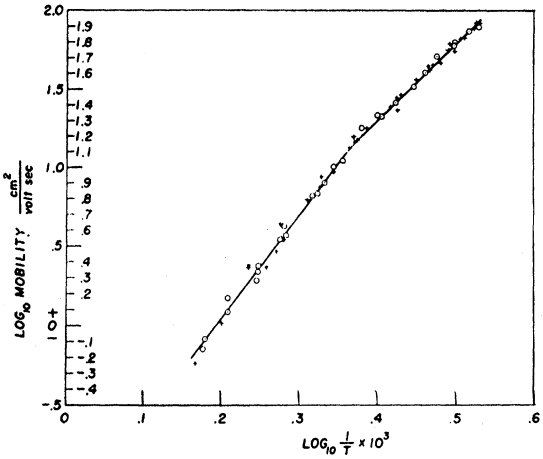

FIG. 5. Mobility as a function of temperature for a well-aged specimen of cuprous oxide. The data are taken from Fig. 3. The low temperature part of the curve shows a T^{-5} dependence, and changes to a T^{-7} dependence beyond 150°C.

Finally, the author wishes to express his sincere appreciation to Professor F. Seitz for his helpful advice and criticism, and to Drs. A. W. Lawson, R. J. Maurer, and S. Pasternack for many stimulating discussions on the interpretation of the data.