allowed to get to the point, there was a sharp explosion and the black deposit turned rust-colored. This suggests that a nitride of iron was formed which is unstable in air.

In some later experiments, it was found that drawing a current of about 0.6 to 2.0 milliampere in mixtures of hydrogen and nitrogen produced ammonia which gave a strong odor if the tube was opened, and this ammonia behaved as an electron-attaching impurity deconditioning the tube. After ammonia had been formed in such a mixture, reduction of current to 0.3 milliampere decomposes the ammonia and conditions the tube again. Opening the tube, no odor of ammonia could be detected.

TABLE II. Composition of gases and mobility of electrons.

Composition	K
100% H_2	7.6×10^5 e.s.u.
30% H_2+70% N_2	7.8
10% H_2+90% N_2	6.9
3% H_2+97% N_2	6.8
1% H_2+99% N_2	6.2
0.3% H_2+99.7% N_2	5.7
0.1% H_2+99.9% N_2	5.0
100% N_2	3.9

In mixtures containing 1 percent or less of hydrogen, the wire end becomes white hot at currents which produce ammonia and it may be that the formation of ammonia is thermal.

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Hall Effect and Conductivity of Cuprous Oxide

STEPHEN JAMES ANGELLO
Randal Morgan Laboratory of Physics, University of Pennsylvania, Philadelphia, Pennsylvania
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Measurements of the Hall constant and conductivity of cuprous oxide show that the exponential law of temperature dependence is not obeyed. It is shown that the departure from this law is caused by a loss of conduction holes with time, and an anomalous decrease in the mean free path in the vicinity of 100°C. An experiment is described which indicates that the rate of aging at 100°C is increased by the application of an electric field.

INTRODUCTION

THE purpose of this paper is to give data on the Hall effect and conductivity of cuprous oxide which contribute to the understanding of the mechanism of electrical conduction in this substance.

It is generally believed that cuprous oxide containing a stoichiometric excess of oxygen is a semiconductor. Semiconductors are substances which possess a conductivity which is intermediate between that of insulators and metals. Furthermore, their conductivity approaches zero as the temperature approaches absolute zero. The published literature on semiconductors is extensive. Good accounts of their properties are given by F. Seitz[1] and N. F. Mott and R. W. Gurney.[2]

The application of a magnetic field to a substance carrying an electronic current causes several electrical and thermal phenomena,[3] of which the most important is the isothermal Hall effect. The Hall effect is a rearrangement

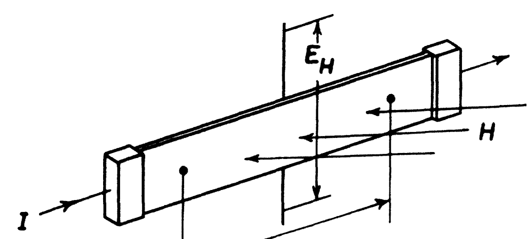


FIG. 1. Schematic diagram showing the electrical connections used in the measurements of Hall effect and conductivity in cuprous oxide. E_H, Hall voltage. E_C, conductivity voltage. H, magnetic field. I, sample current.

[1] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 62 ff. and 186 ff.

[2] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford, 1940), pp. 153 ff.

[3] For a review see A. Sommerfeld and N. H. Frank, Rev. Mod. Phys. **3**, 1 (1931).

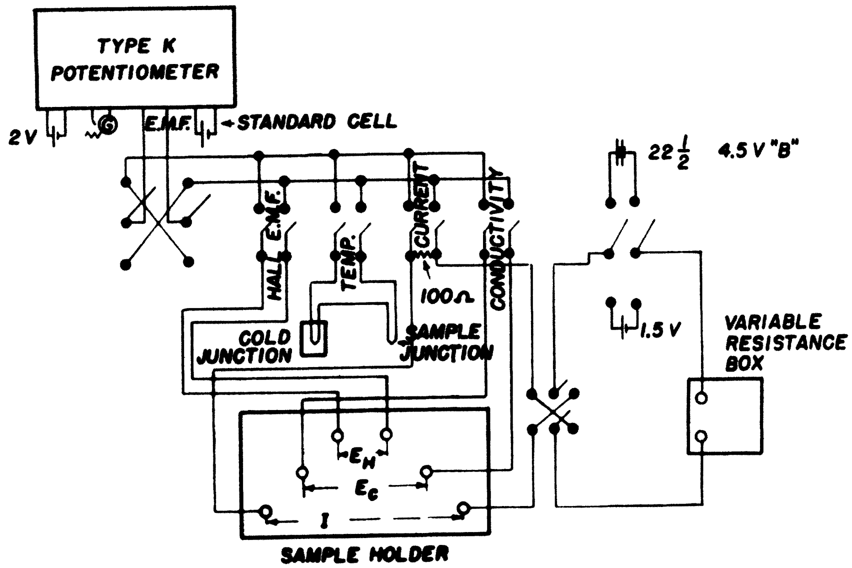


FIG. 2. Circuit diagram of the apparatus.

of the equipotential surfaces in a solid carrying a current, caused by the application of an external magnetic field perpendicular to the current flow. Thus, if the conductor be a flat strip, such as that shown in Fig. 1, in which the current flow is along the length, the application of a magnetic field perpendicular to the strip will cause the equipotential surfaces to shift from positions perpendicular to the axis of the strip to those making a slight angle with the original positions. As a result of this shift, two points situated at opposite edges of the strip which are initially at the same potential will be at different potentials after the application of the magnetic field. This difference of potential is known as the Hall e.m.f. The magnitude of the shift is proportional to the magnetic field strength and the current density. The constant of proportionality is known as the Hall constant. A simple theory[1] of the Hall effect shows that the Hall constant R is given for a semiconductor by the equation

$$R = \frac{3\pi}{8} \frac{1}{ne},$$

where n is the number of electrons per unit volume and e is the electronic charge.

In cuprous oxide the sign of R is positive, meaning that the current carriers are positively charged. This anomalous result was first obtained by W. Vogt.[4] A satisfactory explanation is given by the band theory of solids.[1] In cuprous oxide small regions of electron deficiency are mobile, and play an important role in the conduction. A region of electron deficiency behaves like an electron with a positive sign.

In a study of electrical conduction in a solid, the Hall effect is an important quantity. From the equation above it can be seen that a knowledge of the isothermal Hall coefficient yields the number of conduction electrons per unit volume and their sign. The conductivity is given by the relation

$$\sigma = \text{Constant} \times nl,$$

where l is the mean free path. Knowing n, σ, and the constant, one can calculate the mean free path l. Finally, it can be shown that the mobility of the conduction electrons is given by the equation

$$\bar{v} = R\sigma.$$

Notable researches on the Hall effect in cuprous oxide have been carried out by E. Engelhard,[5] W. Vogt,[4] and H. Dünwald and C. Wagner.[6] Many other references may be found in bibliographies in these papers.

[4] W. Vogt, Ann. d. Physik **7**, 183 (1930).
[5] E. Engelhard, Ann. d. Physik **17**, 501 (1933).
[6] H. Dünwald and C. Wagner, Zeits. f. physik. Chemie **B22**, 212 (1933).

APPARATUS

To measure the Hall effect in cuprous oxide it is necessary to have a device which will measure voltage of the order of 10 millivolts without disturbing the electrical system. A very satisfactory instrument is the Leeds and Northrup Type K potentiometer. The conductivity was determined by measuring the current through the sample and the corresponding voltage drop between two points 1.25 inch apart in the line of current flow. The temperature of the sample was determined by a copper-constantan thermocouple fastened to the cuprous oxide with Scotch tape. All of these quantities involve voltage measurements, and they were made with the same potentiometer and a switching system. The circuit diagram is given in Fig. 2.

With the apparatus used, it was possible to measure the Hall effect and conductivity in the temperature range from −40°C to 100°C with continuous variation. The range of temperature between 25°C and 100°C was obtained by passing dried air through an electric heater, and thence through a box containing the sample. The lower temperatures were reached by bubbling dry air through liquid nitrogen. Various temperatures were obtained by varying the rate of air flow through the refrigerant.

The magnetic field employed was 8850 gauss from an electromagnet. The field was calibrated and shown to be uniform over the area used, by means of a Hartmann and Braun bismuth spiral.

To check the performance of the apparatus, use was made of the relation

$$E_h = RHI/d,$$

where E_h is the measured Hall effect voltage, I is the total current in the sample, and d is the thickness of the sample. First, I was varied keeping H and the temperature constant. This yielded a linear relation between E_h and I. Second, with fixed I and temperature, H was varied. The result was a linear dependence of E_h on H. Ohm's law was checked at room temperature for field strengths of the order of 0.5 volt per cm. As a final check the conductivity of titanium dioxide was measured as a function of temperature from −40°C to 100°C. The logarithm of the conductivity plotted against the reciprocal of the absolute temperature yielded a straight line.

In practice it is impossible to evaporate the Hall contacts on the sample on an equipotential line. To determine the true Hall effect voltage, the following procedure was carried out: (a) The Hall effect was measured with the magnetic field in a certain direction. This yielded V_1 in the equation

$$V_1 = E_h + V_R + e_T,$$

where E_h is the true Hall voltage, V_R is the voltage drop due to improper electrode alignment, and e_T is the contact e.m.f. (b) The measurement was repeated with the magnetic field in the opposite direction. This gave V_2 in the expression

$$V_2 = -E_h + V_R + e_T.$$

E_h was calculated using the relation

$$E_h = (V_1 - V_2)/2.$$

It can be seen from the above equations that the contact e.m.f.'s do not affect the Hall effect determination. The voltage measurement for the calculation of the conductivity is affected by contact e.m.f., and these measurements were corrected by direct determination of the contact e.m.f. In no case did this correction amount to more than 2 percent.

The accuracy of the data presented in this paper is 2 percent or better.

PREPARATION OF THE CUPROUS OXIDE SAMPLES

The cuprous oxide used in this research was prepared by complete oxidation of Chilean

TABLE I.* Analysis of copper strip.

Copper	99.968%
Oxygen	0.029
Sulphur	0.0023
Iron	0.0017
Tellurium	0.0006
Arsenic	0.0005
Selenium	0.0005
Nickel	0.0004
Antimony	0.0003
Lead	0.0003
Silver	0.0001
Bismuth	0.00005

* This analysis was made by the American Brass Company and was communicated to the author by C. C. Hein of the Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania.

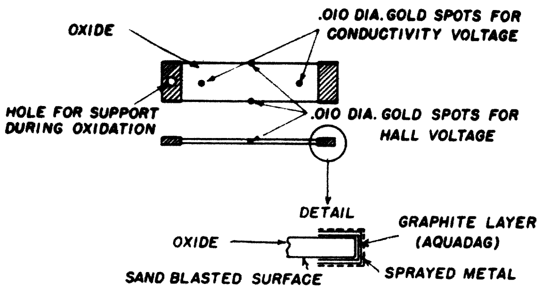
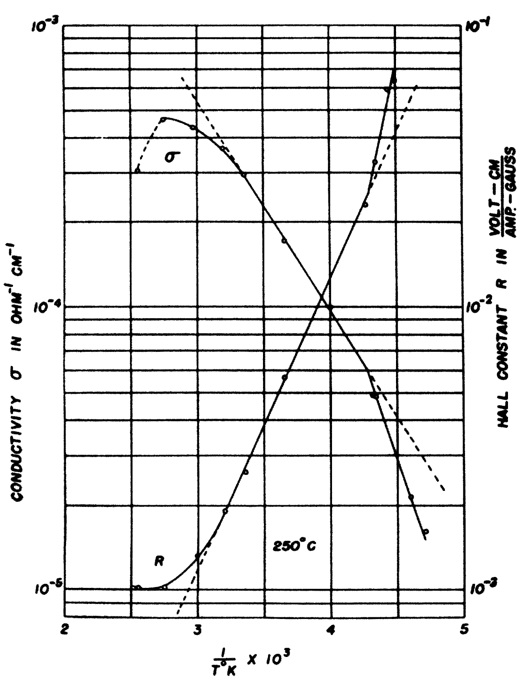


FIG. 3. Structure of the electrical contacts to a typical cuprous oxide sample.

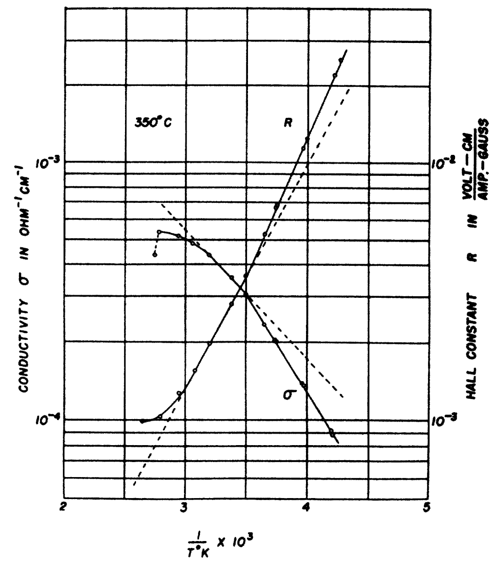
strips $2\frac{1}{4}''$ by $\frac{1}{2}''$ by $\frac{1}{16}''$. An analysis of a typical batch of Chilean copper is given in Table I.

Complete oxidation is accomplished by suspending the clean copper blanks in a furnace at 1000°C in air for 16 hours. After oxidation, the samples are removed from the oxidizing furnace

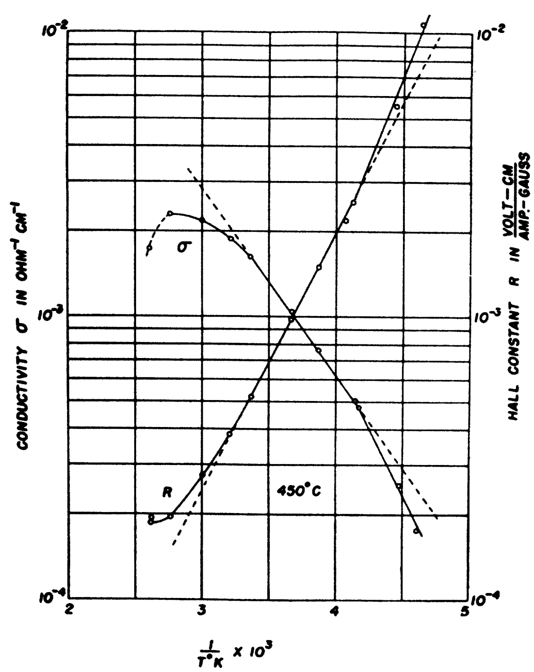
FIGS. 4A–F. Graphs showing the conductivity and Hall constant as a function of reciprocal absolute temperature for cuprous oxide quenched from different annealing temperatures. The discontinuity in the R and σ curves of Fig. 4F was probably caused by the closing of cracks in the sample. The ends of the specimen were fixed, and expansion of the Cu_2O at 100°C was sufficient to account for the effect. The experiment was repeatable, but the data at high temperatures were not reproducible.



A. Room temperature activation energies: $\epsilon_{\sigma 1}=0.148$ ev. $\epsilon_{R1}=0.206$ ev. Low temperature activation energies: $\epsilon_{\sigma 2}=0.292$ ev. $\epsilon_{R2}=0.449$ ev.

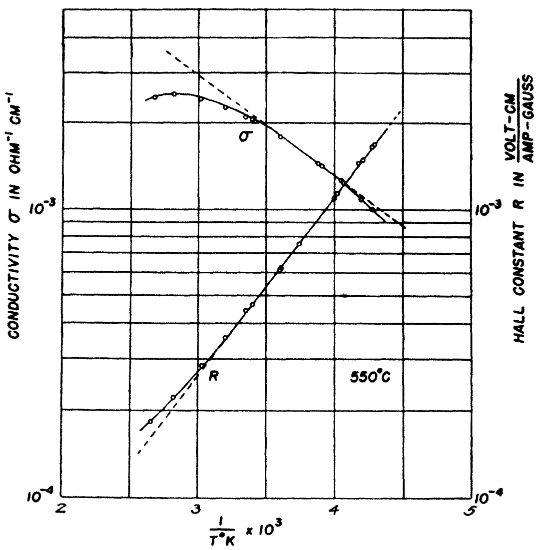


B. $\epsilon_{\sigma 1}=0.102$ ev. $\epsilon_{R1}=0.175$ ev. $\epsilon_{\sigma 2}=0.151$ ev. $\epsilon_{R2}=0.218$ ev.

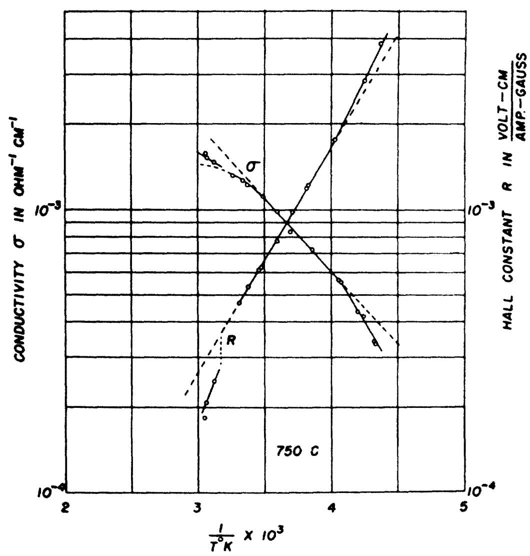


C. $\epsilon_{\sigma 1}=0.132$ ev. $\epsilon_{R1}=0.182$ ev. $\epsilon_{\sigma 2}=0.188$ ev. $\epsilon_{R2}=0.247$ ev.

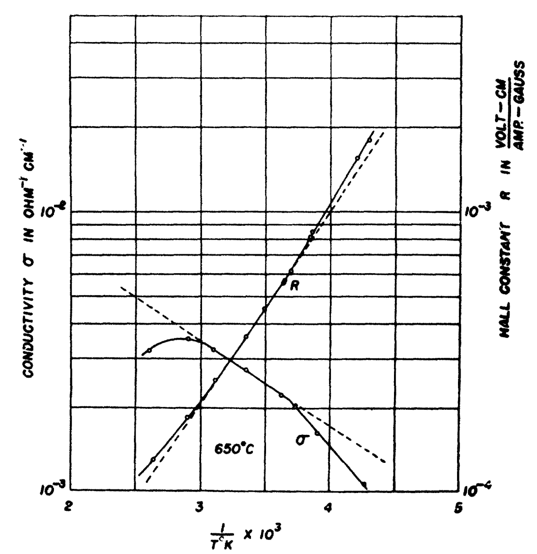
and are placed immediately in an annealing furnace at a lower temperature. Annealing takes place in air for 2 hours, after which the samples are quenched immediately in water at 25°C. The temperature of the annealing furnace has an



D. $\epsilon_{\sigma 1}=0.070$ ev. $\epsilon_{R1}=0.125$ ev. $\epsilon_{\sigma 2}=0.086$ ev. $\epsilon_{R2}=0.125$ ev.



F. $\epsilon_{\sigma 1}=0.104$. $\epsilon_{R1}=0.160$. $\epsilon_{\sigma 2}=0.161$. $\epsilon_{R2}=0.197$.



E. $\epsilon_{\sigma 1}=0.062$. $\epsilon_{R1}=0.140$. $\epsilon_{\sigma 2}=0.107$. $\epsilon_{R2}=0.157$.

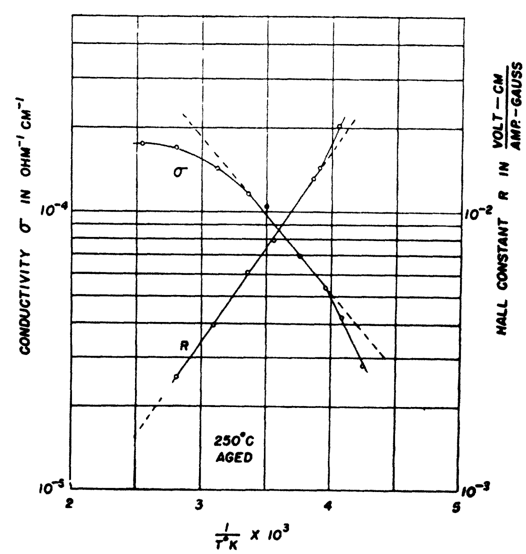


FIG. 5. The conductivity and Hall constant as a function of reciprocal absolute temperature for cuprous oxide quenched from 250°C and aged completely.

important influence on the Hall effect and conductivity of the cuprous oxide. This temperature is specified on all curves in this paper.

Electrodes were prepared for the sample in the following manner:

(a) The oxide was lightly sandblasted to remove cupric oxide scales. It was then dipped in hot sulfuric acid to remove a layer of cuprous oxide, then immersed in nitric acid to remove reduced copper. (b) The end contacts were formed by painting with Aquadag and spraying with hot solder, the rest of the sample being protected with draftsman's Scotch tape. (c) The Hall conductivity electrodes were formed by evaporating gold spots on the sample in an evacuated jar. The structure of the electrodes is shown in Fig. 3.

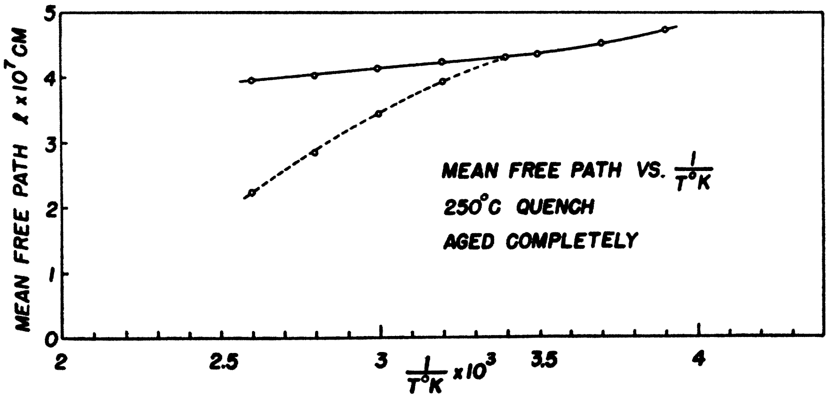


FIG. 6. The mean free path as a function of reciprocal absolute temperature calculated from the data given by Fig. 5. The dotted line is the true mean free path, and the heavy line is calculated assuming a straight line for the conductivity curve of Fig. 5.

RESULTS AND INTERPRETATIONS

The conductivity and the Hall constant of cuprous oxide, treated in the manner previously described, does not obey the exponential law of temperature dependence. Figures 4 A, B, C, D, E, and F show the actual temperature dependence in the range from −40°C to 100°C for samples quenched from different temperatures. The exponential law is obeyed from −40°C to about 35°C. The kinks in the curves in this region have been adequately discussed by Engelhard[5] and Mott and Gurney.[2]

The bends in the R and σ curves in the high temperature region seem to be caused by two factors; namely, a loss of current carriers with *time*, and an anomalous decrease of the mean free path with increasing temperature.

Inspection of the R curves reveals that the Hall constant is larger at 100°C than the simple theory predicts. This indicates that in some way conduction "holes" have been removed from their role as current carriers.

That loss of holes or "aging" is not sufficient to explain the departure from linearity is evident from Fig. 5. The data for this curve were taken on a sample of cuprous oxide which was completely aged; that is, the loss of holes was reduced to a negligible number per unit time. The linearity of the R curve gives evidence that aging has ceased. However, the σ curve shows a distinct bend. Figure 6, which is a plot of the mean free path as a function of temperature' shows clearly that the actual mean free path (dotted line) falls considerably below the mean free path which would be expected if the σ curve were linear.

An interesting experiment was carried out which gives a deeper insight into the nature of aging. Cuprous oxide quenched from 250°C was aged in an oven at 135°C for 5 days. A sample treated in this manner ages only very slightly after 12 hours; hence, in 5 days equilibrium is certainly reached. The sample was removed from the oven and stored at room temperature for 6 months. The values of R and σ for this sample after this time are given by the initial points in Fig. 7. Aging in an oven at 100°C for one hour produced a further drop in conductivity, which ceased in another hour. During the one-hour interval after the fifth hour, an electric field of 30 volts per centimeter was applied to the sample while it was at 100°C. A large decrease in conductivity and a large increase in the Hall constant were the results. Further aging changed these values very little.

The following picture of the mechanism of aging is proposed: All of the samples of cuprous oxide contain cracks which are too small to be visible in the samples quenched from low temperatures (samples quenched from 750°C show visible cracks). By diffusion, excess oxygen in the lattice escapes, leaving small regions of cuprous oxide having a low conductivity. The

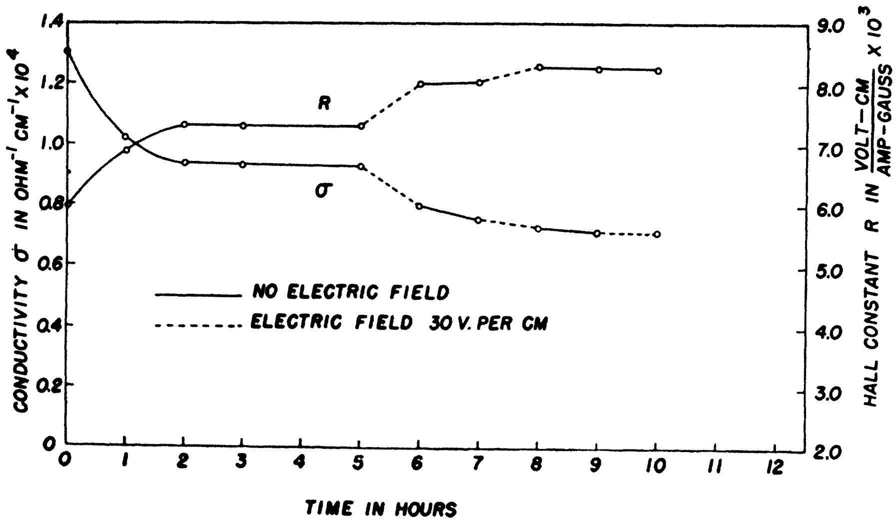


FIG. 7. The Hall effect and conductivity as a function of time for cuprous oxide quenched from 250°C. The dotted curves show aging periods in which an electric field of 30 volts per centimeter was applied.

net effect is to lower the conductivity of the whole sample and increase the Hall constant. Such depleted regions could be replenished by diffusion in an interval of time of the order of 6 months. Further aging at 100°C rapidly depletes them again. The application of an electric field sweeps the current carriers out of the lattice more rapidly than ordinary diffusion processes.

In conclusion I wish to thank Professor F. Seitz of the University of Pennsylvania for guidance and helpful criticism during the work, WPA project 25792 for assistance, Mr. C. C. Hein of the Westinghouse Research Laboratories for cuprous oxide samples and valuable suggestions, and the Westinghouse Electric and Manufacturing Company for financial assistance.