

Carrying out the division in (A4) and retaining only the leading term give

$$n_v = (1/N)Q_1/Q_0, \quad (\text{A6})$$

which is an excellent approximation, since the energy of formation of a vacancy is of the order of 1 ev, and therefore the higher terms in the series are very small.  $Q_0$  is the partition function of a perfect crystal and  $Q_1$  is the partition function of a crystal containing a vacancy.

In the semiclassical approximation,

$$\frac{Q_1}{Q_0} = (N+1) \int \cdots \int e^{-\psi_0/kT} \prod_i dp_j dq_j / \int \cdots \int e^{-\psi_0/kT} \prod_i dp_j dq_j, \quad (\text{A7})$$

where  $\psi_v = \psi_v(p, q)$  is the energy of a crystal containing

a vacancy and  $\psi_0 = \psi_0(p, q)$  is the energy of a perfect crystal. The integrations are carried out over all values of the momenta and coordinates  $p_j$  and  $q_j$ . The factor  $(N+1)$  arises from the fact that  $N$  indistinguishable atoms can be placed in  $(N+1)$  numbered lattice sites in  $(N+1)$  ways so that  $Q_1$  is proportional to  $(N+1)$ .

Combining Eqs. (A6) and (A7) gives

$$n_v = \int \cdots \int e^{-\psi_v(p_j, q_j)/kT} \prod_i dp_j dq_j / \int \cdots \int e^{-\psi_0(p_j, q_j)/kT} \prod_i dp_j dq_j, \quad (\text{A8})$$

where unity has been neglected relative to  $N$ .

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### Surface Mobility of Copper Ions on Cuprous Oxide\*

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This paper reports on the motion of  $\text{Cu}^+$  ion vacancies on the surface of cuprous oxide at room temperature under the application of an electric field. The measurement of the mobility of the  $\text{Cu}^+$  vacancies was made by means of a "time of flight" procedure. The formation of luminescent centers is the unique property of  $\text{Cu}^+$  vacancies that makes them directly observable. The mobility of the  $\text{Cu}^+$  vacancies at room temperature is about  $10^{-11}$  cm<sup>2</sup>/volt-sec. The variation of the mobility with temperatures between 28°C to 55°C is observed. From these data the constants of the diffusion equation  $D = D_0 \exp(\Delta H/RT)$  are computed.  $D_0 = 5 \times 10^{-7}$  cm<sup>2</sup> sec,  $\Delta H = 8100$  calories. The low values obtained for these constants shows that the ionic current follows low-resistance paths formed by the crystal grain boundaries or along the surface of the crystal.

#### INTRODUCTION

THIS paper is a continuation of previously reported work<sup>1</sup> in which the current creep of cuprous oxide rectifiers at room temperature is explained by slow changes in the distribution of  $\text{Cu}^+$  ions. It was reasoned that these ions could move because  $\text{Cu}_2\text{O}$  has ionic vacancies. As it is to be expected, the ionic vacancies give rise to acceptor centers. The acceptor centers allow radiative electron transitions from the conduction band into them, causing emission in the near infrared region.<sup>2,3</sup> The vacancies can therefore be thought of as "luminescent centers" carrying a negative charge.

\* This paper represents a part of the thesis for the Master of Science degree in the field of Electrical Engineering by I. Liberman.

<sup>1</sup> R. Frerichs and R. Handy, Phys. Rev. **113**, 1191 (1959).

<sup>2</sup> J. Bloem, Philips Research Repts. **13**, 167 (1958).

<sup>3</sup> G. F. Garlick, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19, p. 377.

A second reason for assuming ionic motion in  $\text{Cu}_2\text{O}$  at room temperature is based on certain transient properties of the electroluminescence. Frerichs and Handy<sup>1</sup> used a sandwich consisting of a  $\text{Cu}_2\text{O}$  covered plate clamped against a transparent NESA electrode. They observed that placing a dc voltage to this sandwich before an ac voltage is applied causes a transient behavior in the radiation produced by the ac voltage. Transient times on the order of seconds led to the conclusion that the enhancement must be an ionic effect. Thus  $\text{Cu}_2\text{O}$  has the unique property of having some ionic motion at room temperature which can be studied by observing its electroluminescence. This property is utilized in this paper to determine the mobility of  $\text{Cu}^+$  ions on  $\text{Cu}_2\text{O}$  surfaces.

## POINT CONTACT ELECTRODES

The sandwich arrangement used previously is not suitable for measurements of mobility. The Cu-Cu<sub>2</sub>O barrier is parallel to the NESA-Cu<sub>2</sub>O barrier and thus it is impossible to tell at which interface the luminescence originates. Therefore point contact electrodes on a Cu<sub>2</sub>O plate were used to obtain more information about the luminescence. The plates were thin, completely oxidized and translucent and had dimensions of about 0.1×10×20 mm. Two point-contact electrodes of phosphor-bronze (rectifying contacts) were placed on the surface of the plate. An infrared photomultiplier on the other side of the plate observed the electroluminescence. The following experiments were performed using this configuration:

1. In order to determine on which phase of the ac the luminescence is produced, the two point electrodes were separated by 1 cm. An opaque shield between the photomultiplier and the Cu<sub>2</sub>O plate with a pinhole under one of the point electrodes permitted only the radiation from this electrode to reach the photomultiplier. The photomultiplier signal was displayed on one trace of a double-trace oscilloscope while the other trace displayed the ac voltage on the electrodes. It was then observed that the radiation is emitted at the metallic point when it is *negative with respect to the Cu<sub>2</sub>O*. This corresponds to the *forward direction* of the rectifying phosphor-bronze contact.

2. The shield was removed and the point electrodes placed a few mm apart. A dc voltage is connected to the two electrodes. The electroluminescence observed at the negative contact (electrode 1) decreases with time, becoming barely observable after a few minutes. This leads to the conclusion that the luminescent centers are mobile and of an ionic nature as the rate of change of electronic phenomena would be much higher. Reversing the dc results in an identical transient decay of the luminescence at electrode 2. However, while electrode 2 is kept negative and emits radiation, electrode 1 is positive and is "gathering in" the neighboring vacancies. Therefore when the dc is again reversed to its original state a transient enhancement and subsequent decay of radiation is observed at electrode 1.

3. An ac voltage was impressed between the two electrodes. Radiation is then given off when each electrode goes negative with respect to the Cu<sub>2</sub>O. However, the intensity of radiation at one electrode is usually not equal to that at the other electrode. It cannot be expected that the concentration of Cu<sup>+</sup> ion vacancies at both electrodes is equal. This is due to their random distribution obtained during manufacture and due to their low average concentration. By placing two electrodes at random places on the surface of the Cu<sub>2</sub>O a great difference in radiation between the two points is usually observed. After applying a positive dc voltage on the less efficient electrode for a period of minutes

before the ac is applied, the relative amplitudes of the radiation will reverse. The positive electrode has gathered in the neighboring vacancies while the negative electrode has pushed away the vacancies surrounding it. It should be stated that the displacements of the vacancies observed in these experiments are extremely small.

## MEASUREMENT OF MOBILITY

While the experiments using point contacts showed that the vacancies are mobile, they did not give any information on the magnitude of the mobility itself because the distances traveled by the vacancies remained undetermined. A flattened oxidized wire with knife contacts placed perpendicular to the direction of travel along the wire was used to obtain the desired geometry for measuring the mobility (Fig. 1). The wire used (No. 24 AWG) was flattened with a roller to an approximate cross-sectional area of 0.25×0.8 mm and cut to about 2 cm in length. Oxidation was done following a standard procedure.<sup>4</sup>

The initial experiment to measure the mobility is described in a previous report.<sup>5</sup> This experiment has been refined in order to get repeatable results with other samples and to find the temperature dependence of the mobility in order to verify that *surface* rather than *bulk* mobility is measured.

Two platinum wires are placed outside of two zinc knife edges. A dc voltage placed on the platinum wire provides the field for driving the vacancies from the negative to the positive electrode. Periodically (every 30 minutes) the driving field is interrupted and an ac voltage is placed on the zinc electrodes. The resulting radiation is detected on a photomultiplier and the amplitude of the radiation from each knife edge is recorded. (As the radiation occurs when the voltage on the knife edge is negative, only one knife edge emits at any instant.) After some time has elapsed (30–100 hours) the radiation pattern from the knife edge near the negative platinum wire reappears at the other knife

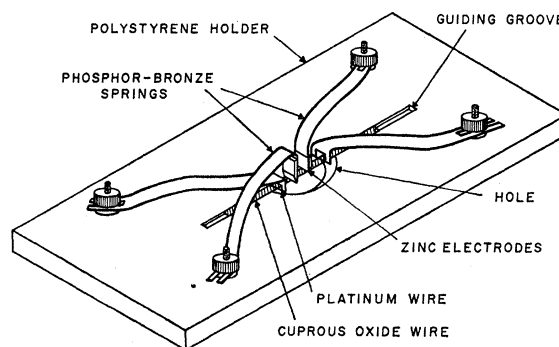


FIG. 1. Cuprous oxide assembly.

<sup>4</sup> F. Weichman, Ph.D. thesis, Northwestern University, 1958 (unpublished). R. Frerichs and F. Weichman, J. Appl. Phys. **29**, 710 (1958), F. Weichman, Phys. Rev. **117**, 998 (1960).

<sup>5</sup> R. Frerichs and I. Liberman, Phys. Rev. Letters, **3**, 214 (1959).

edge. Knowing the time of travel, the average mobility can be computed. The spacing between the zinc electrodes is 75 microns. The surrounding platinum electrodes are 830 microns apart. The dc driving voltage is 135 volts and the ac readout voltage is 50 volts.

Under these conditions it was possible to measure the transient time between electrodes at temperatures from 28°C to 55°C. The lower limit is a practical limit because at still lower temperatures the length of the runs would have to be extended into many hundreds of hours. The upper limit is set by the uniformity of the distribution (explained further on) and the diminishment of the intensity of the luminescence.<sup>1</sup> It was also

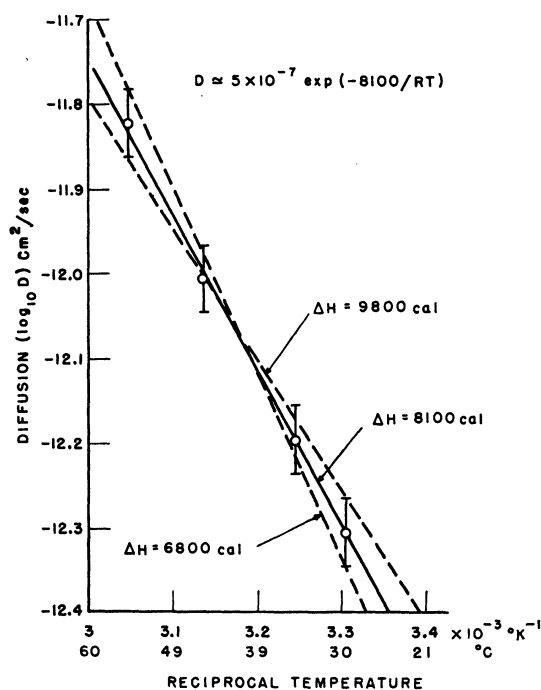


FIG. 2. Diffusion of copper ion vacancies as a function of reciprocal temperature. Dotted curves show extremes of slope due to estimated experimental error.

found that the consistency of the data made it unnecessary to go further.

The results are shown graphically in Fig. 2. The mobility  $\mu$  is calculated as velocity per unit field intensity and the diffusion  $D$  from  $D = \mu kT/e$ . From the slope and intercept of this line the following analytic equation is obtained:

$$D = 5 \times 10^{-7} \exp(-8100/RT).$$

#### EXPERIMENTAL PROCEDURE

##### Vacuum Apparatus

The holder was placed inside a vacuum chamber as shown in Fig. 3. A copper heating mantle with Nichrome

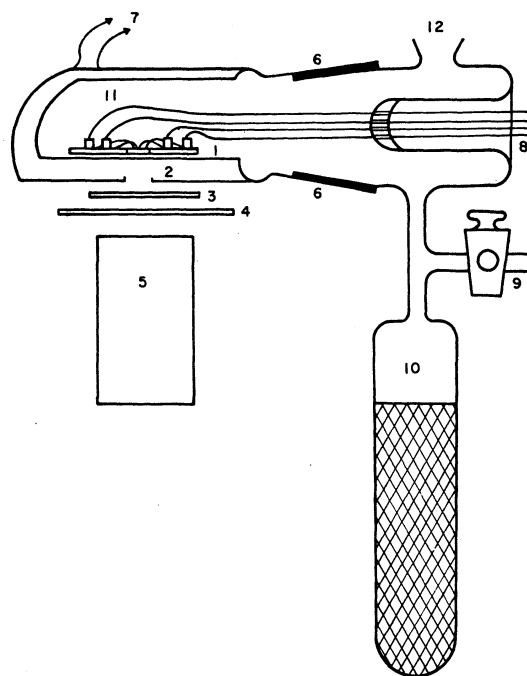


FIG. 3. Vacuum chamber: 1, cuprous oxide assembly; 2, heating mantle; 3, shutter; 4, filter; 5, photomultiplier tube; 6, vacuum wax seals; 7, nichrome wire leads; 8, leads to cuprous oxide; 9, tee stopcock; 10, charcoal trap; 11, evacuated section; 12, thermocouple vacuum gauge joint.

wire heating coils controlled with a temperature controller provided the desired temperatures. The chamber was kept evacuated by a charcoal trap immersed in liquid nitrogen. Thus the possible formation of a CuO surface layer due to the reaction  $2\text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4\text{CuO}$  was eliminated. This reduced the radiation fluctuation considerably.

##### Gating Circuit

For every cycle of ac two pulses of radiation were obtained; one from each zinc knife edge when the voltage on the individual knife edge was negative with respect to the  $\text{Cu}_2\text{O}$ . The radiation from both knife edges was picked up by the same photomultiplier tube and thus only one signal of radiation intensity resulted. The knife edges were so close together that even with elaborate optical equipment it would have been difficult to direct the individual radiation to two separate photomultipliers. The ac signal had a frequency of 200 cps. The change in the amplitudes of these two trains of pulses with respect to time had to be observed. As the ionic mobility at room temperature is very small the duration of the experiment extended from 30 to 100 hours.

The following circuit was used (Fig. 4). The ac signal taken directly from the oscillator is connected to input No. 1. It is amplified and the output is then taken from an inverter in order to obtain an ac signal

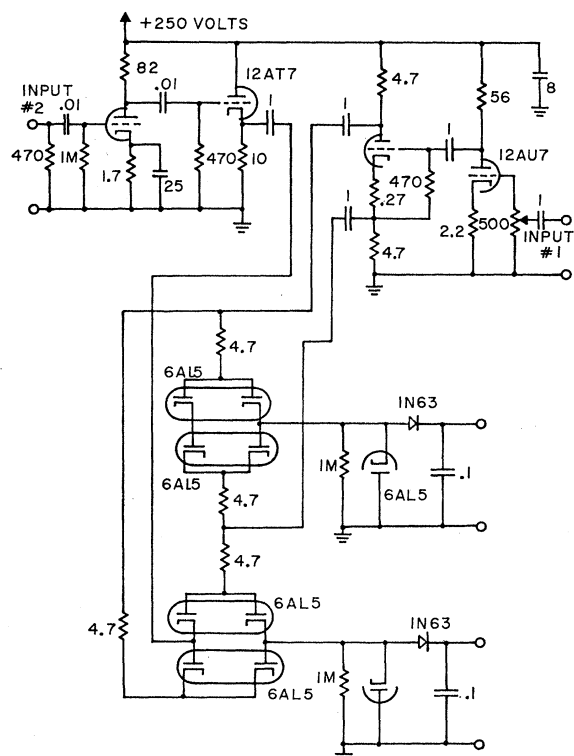


FIG. 4. Pulse separation gating circuit: all resistance in kilohms and capacitance in microfarads unless specified otherwise.

that is symmetrical with respect to ground. This condition is necessary for the proper operation of the gating diodes. The signal from the photomultiplier tube is placed on input No. 2. This signal is first amplified and then connected to a cathode follower in order to obtain a lower output impedance. The signal from the photomultiplier tube now interacts with the ac signal at the diodes. When the upper set of diodes are conducting, the lower ones are not, and vice versa. Thus the light signal has been separated into two signals as desired.

The data were recorded on the Sanborn Recorder making the process entirely automatic. Diodes (6AL5) were used to restore the dc level of the light pulses, and a semiconductor diode and capacitor were used as a peaking circuit to obtain high signal to noise ratio for recording purposes. The capacitor of the peaking circuit was selected to give between pulses of radiation a decay through the reverse resistance of the semiconductor diode of approximately 10%. Thus over a period of a few seconds, the average value of light intensity was accurately reproduced.

This circuit was used in conjunction with a timer-controlled microswitch, a stepping relay, delay relay, and other relays in order to obtain the following sequence of operations. The period of the timing sequence was 30 minutes. For all but two seconds of this time only the driving field was applied to the

platinum electrodes. During the remaining two seconds the driving field was removed, the ac voltage was applied to the zinc electrodes, the photomultiplier was turned on, and the Sanborn Recorder motor circuit was closed, enabling the two-channel recorder to record the magnitude of the luminescence at each knife edge.

### Correlation Technique

In order to know the time of travel between the zinc electrodes, one has to compare the radiation pattern at one zinc electrode with the radiation pattern at the other electrode at a later time. Unfortunately, some difficulties make such an experiment less than ideal (Fig. 5). Each pair of figures is a plot of the radiation as a function of time on each point contact. Figure 5(a) is the ideal case. At time  $A$  a burst of radiation appears at one knife edge. At time  $A'$  an identical burst appears at the other knife edge. The time  $(A'-A)$  is then the time necessary to move the vacancies over the distance between the two knife edges. Figure 5(b) shows what one can actually hope to expect. It is unlikely, if not impossible, for the vacancies to be located within sharply confined boundaries as in Fig. 5(a), since the sharper the gradient of the distribution vacancies the greater will be their self-diffusion. Figure 5(c) is a logical continuation of Fig. 5(b). During the time the vacancies travel from one knife edge to the other, some self-diffusion will occur independent of the field if a concentration gradient exists. Thus some vacancies will not move at the same velocity as others. The characteristic curve at one knife edge will then not coincide exactly with that at the other. This makes it difficult to see the exact correlation between curves. One is also faced with the problem of determining whether the time of travel used in calculating the mobility is  $A'-A$  or  $B'-B$  or some intermediate value. Fortunately, the concentration gradients were not very large and the diffusion constant is so small that the uncertainty in time was under 10% of the total time of travel. At the highest temperature used, the diffusion constant became large enough to make back diffusion quite pronounced so that comparisons between curves became difficult. A typical portion of a good correlation at room temperatures is shown in Fig. 5(d).

### CONDITIONS FOR ELECTROLUMINESCENCE

The ac voltage is used for measuring the vacancy distribution at the inner electrodes but should not move them appreciably. Therefore, a small ac voltage is desirable. Also, with low voltage the vacancies that are excited are nearer to the probes. Thus the measurement of the distances is more accurate. Initially phosphor-bronze electrodes were used to excite  $\text{Cu}_2\text{O}$ . They were changed to zinc, a lower work function metal, after a study of the luminescent model was made.

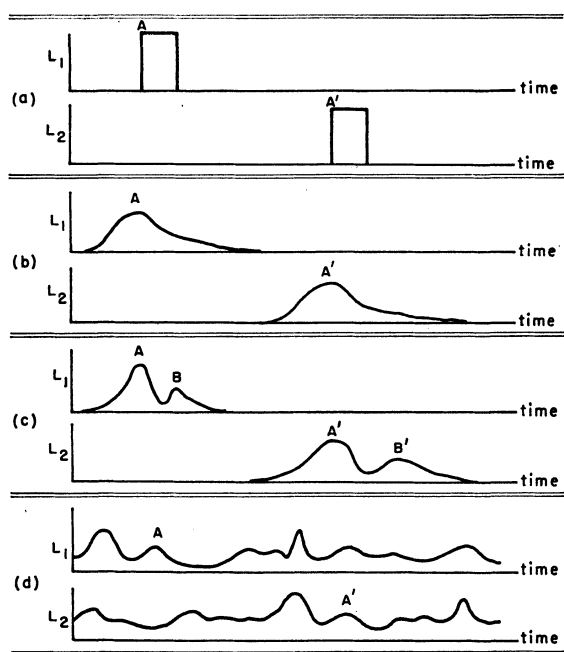


FIG. 5. Electroluminescence as a function of time for various vacancy distributions.

The two zinc knife edges on the cuprous oxide wire form rectifying contacts on a  $p$ -type semiconductor placed back to back. Regardless of the direction of the applied field, there is one reverse-biased and one forward-biased barrier. For electroluminescence to occur, electrons must fall from the conduction band into the luminescent centers in the forbidden band which are caused by the  $\text{Cu}^+$  vacancies.<sup>2,3</sup> A luminescent center is a  $\text{Cu}^+$  vacancy whose negative charge has been neutralized by recombination with a hole in the valence band. The radiative transition of electrons from the conduction band into this luminescent center then restores the effective negative charge of the vacancy. Therefore it is proposed that if the vacancies are present, the necessary condition for luminescence to occur is a sufficient number of electrons in the conduction band. Cuprous oxide is a  $p$ -type semiconductor with a forbidden energy gap of about 2.3 eV.<sup>8</sup> It then appears that only a few electrons could reach the conduction band through thermal agitation or field effect. Therefore it is proposed that the electrons must be injected into the conduction band by the metallic contacts.

The experimental basis for this hypothesis lies in the following observations on this material. A low-work-function metal gives greater luminescence than high-work-function metals. The radiation is emitted at the contact rather than throughout the bulk material. This was observed by means of an infrared image converter. The radiation is emitted when the voltage is negative on the metal contact with respect to the cuprous oxide. This corresponds to the *forward* direction of the rectify-

ing junction. Carrier injection explains these observations.<sup>6</sup>

#### DIFFUSION OF $\text{Cu}^+$ IN CUPROUS OXIDE

The mobility of  $\text{Cu}^+$  ions in  $\text{Cu}_2\text{O}$  at high temperatures had been previously studied experimentally. Two different techniques were used and the results agree quite well both experimentally and theoretically. The first comprehensive experiments are those of Dunwald and Wagner.<sup>7</sup> They derived the ionic mobility  $\mu$  from measurements of the transport number  $\tau$ , the electrical conductivity  $\sigma$ , and the number of vacant sites  $n_i$ :  $\mu = \sigma\tau/en_i$ .

A second method for measuring the mobility of  $\text{Cu}_2\text{O}$  is an indirect one. It is based on the Nernst-Townsend-Einstein relationship  $eD = \mu kT$ , where  $D$  is the ionic diffusion. The diffusion can be measured by measuring the rate of oxidation of the copper. To measure the diffusion directly, Bardeen, Brattain, and Shockley used the radioactive tracer technique.<sup>8</sup>

Additional work on the measurement of diffusion using radioactive copper tracers was performed by Castellán and Moore<sup>9</sup> and Moore and Selikson.<sup>10</sup> Their contribution was in part to verify the values of diffusion of Wagner and Shockley at 1000°C as well as to find the diffusion of  $\text{Cu}^+$  ions at 900°C and 800°C. At these lower temperatures the cuprous oxide formed is not equilibrium cuprous oxide so that the diffusion coefficient computed is not necessarily that of equilibrium cuprous oxide. It is rather that for the particular slab of cuprous oxide formed on oxidation. The values of diffusion at the three different temperatures were plotted logarithmically as a function of reciprocal temperature and found to be on a straight line. From this line  $D$  was found to be  $0.0358 \exp(-37\,000/RT)$   $\text{cm}^2 \text{ sec}^{-1}$ <sup>9</sup> and  $0.0436 \exp(-36100/RT)$   $\text{cm}^2 \text{ sec}^{-1}$ <sup>10</sup> over the temperature range studied. Extrapolation of the volume diffusion down to room temperature (Fig. 6) leads to prohibitively long diffusion times under the conditions used in the present experiments. However, the experiments of Frerichs and Handy<sup>1</sup> have shown that ionic diffusion influences the electroluminescence in  $\text{Cu}_2\text{O}$  even at room temperature.

From the low value of the heat of activation derived from our measurements it can be concluded that the  $\text{Cu}^+$  ions do not diffuse through the bulk material (*volume diffusion*). Such low values for the heat of activation can be expected for surface diffusion or grain boundary diffusion as a special case. At this time

<sup>6</sup> K. Lehovec, C. A. Accardo, and E. Jamgochian, *Phys. Rev.* **83**, 603 (1951).

<sup>7</sup> H. Dunwald and C. Wagner, *Z. physik. Chem.* **B22**, 212 (1933).

<sup>8</sup> J. Bardeen, W. H. Brattain, and W. Shockley, *J. Chem. Phys.* **14**, 714 (1946).

<sup>9</sup> G. W. Castellán and W. J. Moore, *J. Chem. Phys.* **17**, 41 (1949).

<sup>10</sup> W. J. Moore and B. Selikson, *J. Chem. Phys.* **19**, 1539 (1951).

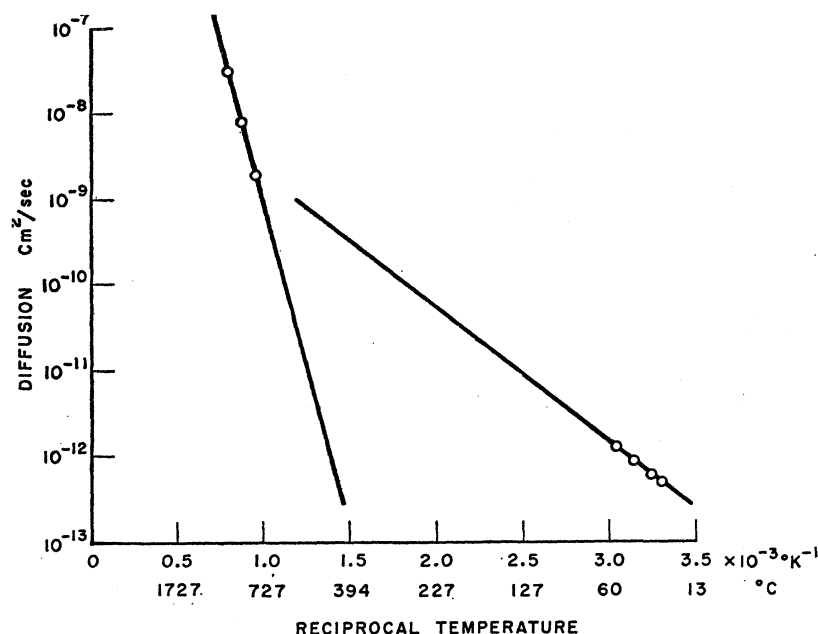


FIG. 6. Comparison of data of diffusion vs  $1/T$  with results obtained at high temperature by Castellan and Moore.

we cannot distinguish between these two effects. These conclusions are based on the work of Langmuir<sup>11</sup> who first observed with W and Th the change from volume, to grain boundary, to surface diffusion with decreasing temperature.

In the present literature only a beginning has been made in the investigation of these phenomena.<sup>12</sup> No information is available for semiconductors and ionic or covalent crystals.<sup>13</sup> Our experiments have been made on polycrystalline material with rather fine grains. On material consisting of larger individual crystals it could be determined whether the motion of the  $\text{Cu}^+$  ions follows the surface or the grain boundaries. At low temperature the surface diffusion follows certain paths on the crystal surface which are determined by the directions having minimum transition energy.<sup>12</sup> At higher temperatures this directed motion will become

more and more randomly oriented. Cuprous oxide surfaces with large crystallites of known orientation should be well suited for the study of the directed diffusion. Such an experiment involving fine point contacts placed on the surface of a single crystal or on the grain boundaries between larger crystals of known relative orientation will provide valuable information in this field. This experiment is presently being prepared.

#### CONCLUSION

The method presented is capable of determining small changes in the distribution of  $\text{Cu}^+$  vacancies so that they can be used to study the surface diffusion in  $\text{Cu}_2\text{O}$  at room temperature. As this method employs electroluminescence it is limited to the temperature range where this can be observed. The presence of  $\text{Cu}^+$  vacancies is directly determined in well-defined locations through the electroluminescent properties of this material. This method, as applied to the measurement of the surface mobility of  $\text{Cu}^+$  vacancies in  $\text{Cu}_2\text{O}$ , is presently the only means available for studying such small surface mobilities.

<sup>11</sup> J. Langmuir, J. Franklin Inst. **217**, 543 (1934).

<sup>12</sup> Committee on Solids, *Imperfections in Nearly Perfect Crystals* (John Wiley & Sons, New York, 1952), p. 470.

<sup>13</sup> K. Hauffe, *Reaktionen in und an festen Stoffen* (Springer-Verlag, Berlin, 1955), p. 408.