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The Electrical Conductivity of Zinc Oxide

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The electrical conductivity of zinc oxide for an average sample obeys the following equations, $\sigma = 10^{-2} \exp(-2\times 10^{-2}/kT)$ ohm^{-1} cm^{-1} for $T < 25$°C and $\sigma = 10^2 \exp(-7\times 10^{-1}/kT)$ ohm^{-1} cm^{-1} for 400°C $< T <$ 700°C. The conductivity in the lower temperature range is believed to be due to the ionization of interstitial zinc atom pairs, whose ionization energy is 2×10^{-2} volt or less. Conductivity of this type reaches saturation about room temperature. In the higher temperature range the conductivity is caused by the ionization of single interstitial zinc atoms, whose ionization energy is 7×10^{-1} volt. At 800°C the conductivity of this type begins to reach saturation. Hall effect measurements show the free electron density to be about 10^{15} cm^{-3} at room temperature. The fraction of pairs existing is 10^{-3} which is a factor of ten larger than the *a priori* probability.

Introduction

The electrical properties of zinc oxide have been investigated by many observers, particularly by Baumbach and Wagner[1] above room temperature and by Fritsch[2] at and below room temperature; the latter also gives a rather complete bibliography. Zinc oxide is an excess electron semi-conductor; this is established from the sign of the Hall coefficient, the sign of the Seebeck e.m.f., and the dependence of the conductivity on the oxygen pressure. Most observers have found that the electrical conductivity, σ, obeys the usual equation for semi-conductors, $\sigma = Ae^{-\epsilon/kT}$, in two temperature ranges. Up to room temperature A is approximately 10^{-3} to 1 ohm^{-1} cm^{-1} and ϵ, the activation energy, is between 0.01 and 0.1 volt; the variation depends on the past history of the sample and the observer. The second temperature range in which the law is obeyed is from 400°C to 700°C. Here A is some power of ten larger for the same sample with the values ranging from 10^{-1} to 10^2 ohm^{-1} cm^{-1}, while the value of ϵ, varies from 0.5 to 1.5 volt. In the intermediate temperature range of 100°C to 400°C the conductivity follows no simple relationship and in fact it sometimes increases with decreasing temperature. It is with the investigation of these effects that the present paper is concerned.

Apparatus and Measurements

Since the conductivity is a function of oxygen pressure, temperature, past history and, in some types of measuring circuit, of the contact resistance of the electrodes, considerable care must be used in separating the dependence of the conductivity on these effects. The conductivity was measured in the lower temperature range by the potentiometer-probe method whose circuit diagram is shown in Fig. 1, which also shows the Hall effect connection. This method limits the effect of contact resistances to a mere reduction of the sensitivity of the galvanometer. The overall resistance of these samples was determined by measuring the voltage applied to the end electrodes, and from this it is possible to determine the contact resistance. These samples were rectangular in shape being approximately $0.15 \times 0.75 \times 4.5$ cm^3. Zinc electrodes were evaporated on the ends and at the Hall and conductivity

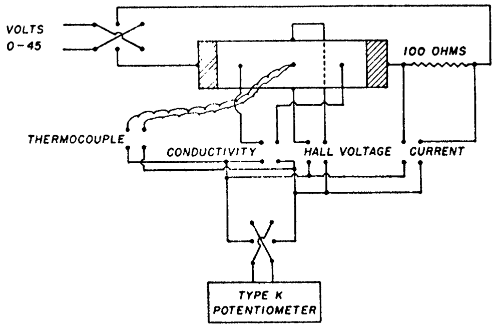

FIG. 1. Circuit diagram for Hall e.m.f. and conductivity measurements at room temperature.

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[1] H. H. v. Baumbach and C. Wagner, Zeits. f. physik. Chemie **B22**, 199 (1933).
[2] O. Fritsch, Ann. d. Physik **22**, 375 (1935).

contact points. Zinc electrodes were found to give a smaller contact resistance than gold or Aquadag. The apparatus for the measurement of the Hall effect was conventional in design and will be described in detail in a paper by S. J. Angello which will shortly be published. A field of 8800 oersteds was used, being reversed to eliminate thermal e.m.f.'s at the contacts and lack of alignment of the electrodes. Sintering at 1200°C for twelve hours in air increased the density from about 65 percent to about 95 percent of the value for single crystals. The samples were allowed to cool in air after removal from the furnace.

From the conductivity and the measured Hall coefficient, R, defined as $E=R(\mathbf{I}\times\mathbf{H})/t$ where E is the Hall em.f., $\mathbf{I}$ the longitudinal current, $\mathbf{H}$ the magnetic field and t the thickness of the sample, one can calculate the mean free path, the density and the mobility of the free electrons on the basis of the free electron theory which makes the following predictions.[3]

$$R=-\frac{3\pi}{8}\frac{1}{n_f ec}.$$

$R\sigma=$ mobility and if $\epsilon\gg kT$

$$\sigma=n_b^{\frac{1}{2}}\frac{4\sqrt{2}}{3}\frac{e^2 l_0}{h^{\frac{3}{2}}}(2\pi mkT)^{\frac{1}{4}}\exp[-\Delta E/2kT]$$
$$=0.024 l_0 n_b^{\frac{1}{2}} T^{\frac{1}{4}}\exp(-\epsilon/kT),$$

$$R\sigma=-\frac{e}{(2\pi mkT)^{\frac{1}{2}}}\frac{\pi l_0}{2c}=\frac{28}{T^{\frac{1}{2}}}l_0,$$

where n_b is the number of bound electrons, n_f the number of free electrons, l_0 the mean free path, $-\Delta E$ the energy of the bound electrons at absolute zero relative to the free electron levels, and c the velocity of light. The other symbols have their usual meaning. Gaussian units are used throughout.

TABLE I. *Aging of zinc oxide at 135°C.*

CONDUCTIVITY	TIME
3.79×10^{-3} ohm^{-1} cm^{-1}	0 minutes
3.73	20
3.69	45
3.65	70

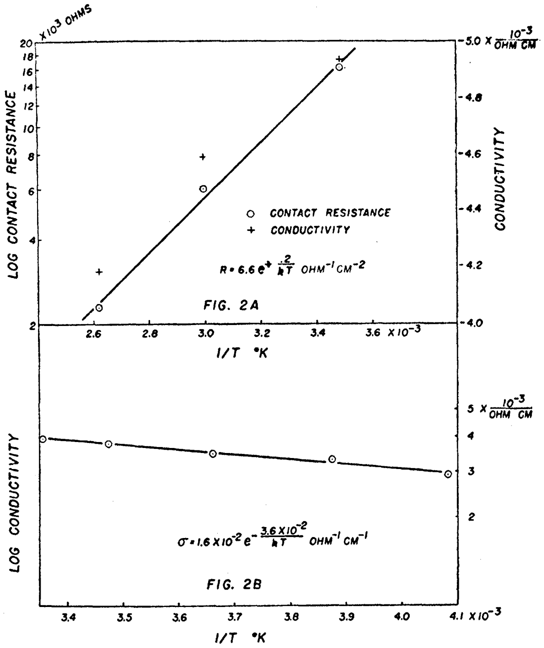

FIG. 2. Contact resistance and conductivity as a function of temperature. (A) Fresh sample; (B) aged sample.

The room temperature conductivity of these fresh samples remained constant over a period as long as a month, but on their initial heating, as Figs. 2A and 3A show, it was generally found that the conductivity decreased with increasing temperature up to 140°C which was the temperature limit of the apparatus. The time required for a run is about an hour. Maintaining the temperature at 135°C caused the conductivity to decrease slowly with time as Table I shows. A relatively rapid permanent change on the first heating must take place. On further temperature changes the conductivity of the aged samples decreased reversibly with decreasing temperature. Figures 2B and 3B illustrate this type of behavior. Below 0°C the conductivity exhibited the normal temperature dependence.

The Hall effect measurements are shown in Figs. 3A and 3B. The same sample is used as in Figs. 2A and 2B but it was sintered again and a new set of contacts was employed. Figure 3A shows that the number of free electrons, as well as the conductivity, decreases with increasing temperature for the fresh sample. Figure 3B indicates that the number of free electrons remains about constant on subsequent temper-

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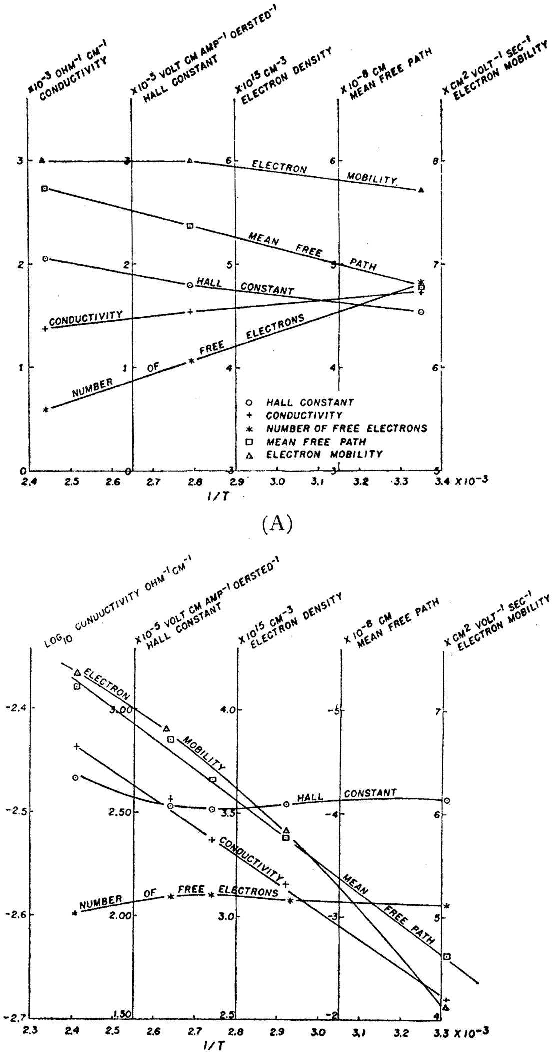
[3] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1940).



(A)

(B)

FIG. 3. Hall effect and conductivity results as a function of temperature. (A) Fresh sample; (B) aged sample.

ature changes. In both cases the mean free path increases with temperature. This is a surprising result. This increase in mean free path may be analogous to the decrease in dielectric strength with increasing temperature that von Hippel[4] and his co-workers report, and the decrease in the number of free electrons may be due to the change in the number of interstitial zinc atoms interacting to form pairs. This will be discussed in more detail later.

For the conductivity measurements at higher temperatures samples were prepared by evaporating zinc on the plane faces of zinc oxide cylinders, 1.1 cm diam. and from 0.2 to 1.0 cm thick. The pill was first sintered in air at 1000°C for 12 hours. Gold was evaporated on top of the zinc to hinder its oxidation during subsequent measurements. Gold foil was placed over the evaporated gold and the pill was inserted between two platinum electrodes. The current through and the voltage across the pill were simultaneously measured. Both the contact resistance and volume resistance decrease rapidly with increasing temperature, but the contact resistance decrease is so rapid that between 250°C and 400°C it is less than 10 percent of the volume resistance for this shape of pill. Above 400°C the volume resistance also decreases rapidly with temperature but it was found that the conductivity was independent of the thickness of the sample within 10 percent, indicating that the contact resistance could be neglected.

Excess semi-conductors form a rectifying boundary with a metal electrode, the direction of high resistance being with the metal negative. A series of pills were prepared with zinc-zinc electrodes; their resistance was measured. One electrode was removed and replaced with an evaporated gold electrode. At 25°C the contact resistance varies from 10 to 150 ohm cm^{-2} with the gold as the positive electrode. When gold is the negative electrode it varies between 10 and 1000 ohm cm^{-2}. Ohm's law was obeyed for voltages over 3 volts, and with all samples the power dissipation had to be kept below 1 watt cm^{-3} to prevent thermal breakdown.

If at 500°C plain gold electrodes were employed and the current was allowed to flow for ten minutes in one direction the conductivity improves by 5 to 10 percent, and upon reversal of the direction of the current it will fall, sometimes quickly and sometimes slowly, to or even below the original value and then it will increase after about thirty minutes to the former high value. This cycle can be continued, but if more than 5×10^3 coulombs are allowed to flow the repetition becomes less exact. Since zinc oxide has a slight ionic conductivity as Wagner has pointed out and which our diffusion measurements confirm, a possible explanation is that at

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[4] A. von Hippel and R. J. Maurer, Phys. Rev. **59**, 820 (1941); A. von Hippel and G. M. Lee, Phys. Rev. **59**, 824 (1941).

500°C the conductivity improves because the zinc "plates" out on the negative gold electrode reducing its rectifying action, but with the reversal of the direction of the current the conductivity falls until the other electrode has been similarly affected. With the additional effect of the zinc returning to the lattice from the positive electrode it is possible to explain the shapes of all the curves that were experimentally obtained. Above 400°C with zinc-zinc electrodes the change in conductivity with time of flow or direction of current was not more than several percent.

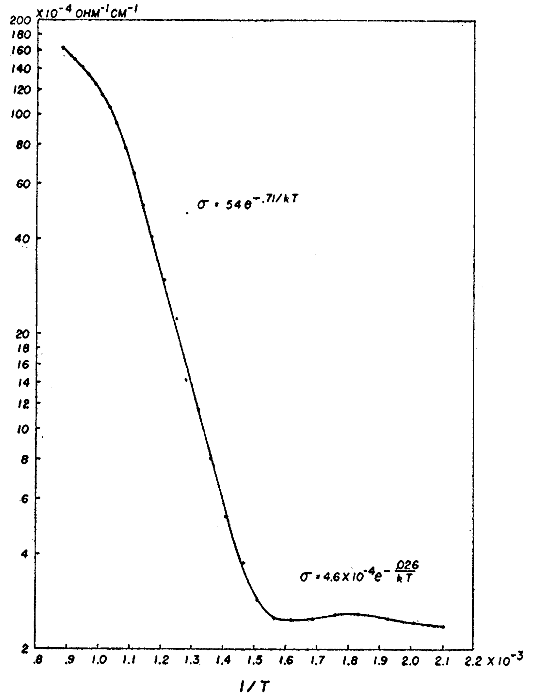

FIG. 4.

The zinc oxide is never in true temperature equilibrium. One pill was kept at a constant temperature, 530°C, and oxygen pressure for six days and after the first day the conductivity decreased continuously at a rate of 3 percent per day. The conductivity is oxygen pressure dependent; Baumbach and Wagner[1] working with poorly sintered samples found $\sigma=f(T)P^{-1/n}$ where $n=4.3$, for the temperature range 500°C to 700°C. If all the electrons of the interstitial zinc atoms are evaporated into the conduction band, consideration of the free energy[3] predicts an equilibrium dependence of $\sigma=Cp^{-\frac{1}{4}}e^{-\epsilon'/kT}$ where ϵ' is the energy required to remove an oxygen atom and form an interstitial zinc ion and a free electron. On the other hand, if only a small fraction of the interstitial zinc atoms lose their electrons and this contribution to the free energy is neglected, we have exactly the same pressure dependence but with different values of C and ϵ', because the conductivity in this case is proportional to the square root of the number of bound electrons. Figure 4 shows the conductivity as a function of temperature for a typical case; the time required for the run is about two hours. The left-hand portion of the curves is very similar to those obtained by Baumbach and Wagner[1] and by Jander and Stamm.[5] The slope of this section is 0.71 volt and that of the right-hand part is 0.026 volt which is in agreement with that obtained by the potentiometer probe method. The question before us is whether all the electrons are free in the high temperature range and the change in conductivity with temperature is due to a change of the number of interstitial zinc atoms, or whether the number of interstitial zinc atoms remains about the same and the number of free electrons increases. The rate of loss of weight for heating in air is given by Gmelins[6] for the temperature range of 1200° to 1400°C. This loss is due either to the evaporation of oxygen atoms or zinc oxide molecules. To place an upper limit on the number of interstitial zinc atoms formed per hour we shall assume the former to be the process and extrapolate Gmelins' data to 800°C where we find the maximum number of interstitial zinc atoms formed to be 2×10^{14} atoms cm^{-3} hour^{-1}. The number of interstitial atoms calculated from $A=0.24l_0n_b^{\frac{1}{2}}T^{\frac{1}{4}}$ is 10^{18} atoms cm^{-3}. Therefore we see that the number of interstitial zinc atoms could not change appreciably during the two hours it takes to complete a run. This is further confirmed when we observe that for a change in oxygen pressure from 10^2 cm to 10^{-2} cm Hg, the conductivity changes by about 15 percent in the first hour. The change in conductivity with temperature in the high temperature range would

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[5] W. Jander and W. Stamm, Zeits. f. anorg. Chemie **199**, 165 (1931).

[6] Gmelins, Handbuch d. anorg. Chemie, Bd. Zink (Verlag Chemie G.m.b.H., Leipzig–Berlin, 1924).

seem to be due not to the change in the number of interstitial zinc atoms but primarily to the evaporation of additional electrons from the interstitial zinc atoms.

The rate of diffusion of zinc was determined by evaporating some radioactive zinc (Zn^{65}) on one end of a flat zinc oxide cylinder and determining its redistribution after heat treating. This is essentially the method used by Banks.[7] The sections were removed with a piece of emery paper placed against a flat plate in the tail stock of a lathe. Because of the small rate of diffusion, namely, 4×10^{-11} cm^2 sec.$^{-1}$ at 1000°C the accuracy of this method is poor; the error may be as large as a factor of 2. The ionic conductivity of the zinc atoms is calculated from the diffusion coefficient[3] by use of the relation $\sigma = Ne^2D/kT$. Here N is the density of zinc atoms (10^{22} cm^{-3}) and D is the diffusion coefficient. Thus at 1000°C the ionic conductivity should be 5×10^{-7} ohm^{-1} cm^{-1}, and can be neglected in comparison with the electronic conductivity. In these rough experiments D seems to be independent of oxygen pressure.

CONCLUSIONS

The following model is proposed to explain the behavior of zinc oxide. There are very few interstitial zinc atoms until the sample is heated for an appreciable time at, say, 1000°C. The density of interstitial zinc atoms is then about 10^{18} cm^{-3}, most of which remain in their interstitial positions if the sample is cooled quickly (no oxygen returns). The exact number depends on the temperature, oxygen pressure, time of sintering, and rate of cooling. With this density the interstitial atoms are about 10^{-6} cm apart, too far for appreciable interaction of these atoms. However, it is possible that the interstitial zinc atom and its electron are behaving as if they were in a continuous medium of dielectric constant k; the potential between them will be lowered by the factor k and the ionization energy by k^2 if the zinc atom is considered hydrogen like. Thus the ionization energy for zinc may be reduced from 9.4 volts to about one volt, and thus make $\epsilon = \Delta E/2 = 0.5$ volt, which is in experimental agreement with the observed 0.7 volt considering the crude model we have pictured. Now some interstitial atoms, say about 10^{-3} of them (this is the average ratio of the low temperature conductivity to high temperature saturation value) might be so close that they will interact to form a stable pair. The ionization energy of the pair will be much lower than 0.7 volt, because of "promotion" and will be comparable with the value of 0.02 volt observed for the low temperature range. The presence of such pairs will explain the behavior of the conductivity at room temperature and below. If the density of interstitial atoms is 10^{18} the fraction that would be neighbors for a purely random distribution is n_b/N or 10^{-4}; a slight attraction between atoms will explain the observed value of 10^{-3}. The slight drop in electron density sometimes observed in a fresh sample when the temperature is initially increased is possibly due to the breaking up of these pairs and the recapture of the electron by interstitial zinc ions. After the sample has aged we find the number of free electrons remains about constant from 25°C to 135°C and the mean free path unexpectedly increases. From 400°C to 700°C the conductivity increases because of the evaporation of the electrons from the ordinary interstitial position into the conduction band with an activation energy of about 0.7 volt. The shape of the curve above 700°C is explained by saturation. The number of free electrons determined from the Hall effect is about 10^{15} cm^{-3} at room temperature. We note from Fig. 3B that the conductivity is approaching saturation at high temperatures when the number of free electrons in this case is about 2×10^2 times the room temperature value. The number is probably larger for we have ignored the possibility of a change in the mean free path. This gives a value of 2×10^{17} for the number of interstitial zinc atoms, which is in agreement with the value of 10^{18} cm^{-3} calculated from the relation $A = 0.024 l_0 n_b^{\frac{1}{2}} T^{\frac{1}{4}}$. Thus above 800°C, even though ϵ is large compared with kT we have begun to reach saturation because the large entropy of the free electrons encourages ionization. This does not conflict with the previous argument concerning the oxygen pressure dependence of the conductivity in the temperature range 500°C to 700°C where the

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[7] F. R. Banks, Phys. Rev. **59**, 376 (1941).

number of free electrons is still small compared with the number of interstitial zinc atoms and the free electron contribution to the entropy is negligible in comparison with that of the interstitial zinc atoms.

In conclusion I wish to thank M. D. Earle, S. J. Angello, and members of Works Progress Administration Project 25792 for assistance in observation. I am also deeply indebted to Dr. F. Seitz for his many helpful discussions of the theoretical side of the problem in which he suggested many of the arguments presented here.

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Variation of the Magnetic Properties of Antimony with Electron Concentration

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The principal magnetic susceptibilities of single crystals of pure Sb and solid solution alloys of Sb with Sn, Ge, Pb, and Te have been determined. It is found that as the percent of alloying metal increases the susceptibility perpendicular to the trigonal axis ($\kappa_\perp$) changes but little and remains diamagnetic. On the other hand the susceptibility parallel to this axis ($\kappa_{||}$) decreases sharply in magnitude and, in the case of Sn and Ge, changes from diagmagnetic to paramagnetic beyond 1.17 atomic percent Sn and 1.25 atomic percent Ge. This result permits us to calculate the number of electrons which overlap into the second Brillouin zone in antimony as 10^{-2} electron per atom. The bearing of these results on the current theory of metals is discussed.

In recent years substantial advances in the theory of the solid state have been made, and at the present time we have at least a qualitative understanding of many of the properties of metals. The position on the quantitative side is less satisfactory and comparatively few experiments have been performed which can be considered to be in good agreement with theory.[1] Among the kind of experiments which could be considered suitable for a quantitative check on the theory are those dealing with magnetic susceptibility, since it is known that this quantity should depend primarily on temperature and electron concentration. This sort of experiment is particularly favorable since, in many elements, the electron concentration and temperature may be varied independently. In the present work only the effect of varying the electron concentration is studied.

A convenient method of varying this quantity in a given metal is to alloy it with known amounts of another metal whose valence is different from that of the parent substance. However, with few exceptions, the electrons in a metal cannot be considered as "free." Rather, they are coupled to the lattice ions, that is, they move in a potential field due to these ions, which varies in a periodic manner throughout the crystal. Hence in order to vary the electron concentration it is also necessary to ensure that the alloying element does not appreciably disturb the lattice structure of the pure metal to which it is added. This latter condition, of course, can never be perfectly complied with. Nevertheless, it may be closely approximated by choosing the alloying elements such that they form a simple solid solution with the parent metal. In this case the foreign atoms go into the parent lattice by simple substitution, and, provided they comprise only a few percent of the total atoms present they do not materially change either the original lattice type or its parameters.

Antimony was chosen for the present investigation, since it is possible with this element to realize all the conditions imposed above. Elements possessing one less electron per atom than

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* Now with the Corning Glass Works, Corning, New York.

[1] A good modern exposition of the whole subject is to be found in F. Seitz, *Modern Theory of Solids*, (McGraw-Hill, 1940).