The variation in sharpness results in a small variation in the voltage required for a given current as shown in Table I, and any difference in voltage required for the current due to changing the character of collecting surface is less than this random variation between wire ends.

DISCUSSION

In a previous article[2] it was reported from point-to-plane measurements that there is an ionization sheath potential drop which remains approximately constant while the distance to the collector is varied by large amounts.

The observations being reported here show that for the finest points, the charge in front of the tip of the point reduces the field intensity more in those parts of the ionization sheath nearer that space charge in a manner to reduce the ionization current in the forward direction and thus favor the lateral current. This effect is most noticeable at the smallest values of current so it is evident that a very small reduction of field intensity produces a large percentage reduction in ionization current. At the largest values of current, the current is essentially a space charge limited current arising at the hemispherical cap over the tip, and as such the percentage change of field intensity at the tip does not vary so much with angle at the tip.

The heavier wires have dull enough ends to prevent this effect from pushing the discharge back because the field attenuates less rapidly with distance from the tip and there is a less accumulation of charge near the tip.

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[2] W. H. Bennett, reference 1, pp. 995, 996.

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The Electrical Conductivity of Titanium Dioxide

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Experiments on titanium dioxide show that it is an electronic semi-conductor in which the the current carriers are actually free electrons, as contrasted with the hole conduction of the other type of semi-conductor. It is found that the variation with oxygen pressure is that which would be expected if the titanium dioxide decomposes in the following manner: $TiO_2 \rightarrow Ti^+ + O_2 + e^-$. The deviation of the curves at low pressures is probably due to the presence of small impurities in the samples used. It is found that the variation of conductivity with temperature is represented by the formula $\sigma = Ae^{-\epsilon/kT}$. The activation energy ϵ is about 1.7 electron volts. Transport measurements show that the ionic conductivity is less than that which can be measured in these experiments. Measurements of the Hall effect, although not very quantitative, show that the mean free path for the conduction electrons is very small.

INTRODUCTION

The Electrical Conductivity of Titanium Dioxide

RECENTLY much interest has been shown in the mechanism of electrical conduction in solid materials known as semi-conductors. These substances are characterized by the fact that they possess a room temperature resistivity lying between approximately 10^3 and 10^8 ohm-cm, which decreases with increasing temperature. They differ from metals in that their resistance is much higher and that their temperature coefficient of resistance is of the opposite sign. The current in semi-conductors is usually carried by electrons, although ions may carry a large part or all of the current. Substances in which the conduction is principally by ions are spoken of as ionic semi-conductors. Their resistance in general is slightly lower than that of the electronic semi-conductors.

There are three well-known means of distinguishing between electronic and ionic conductivity. These are: Hall effect measurements, thermoelectric effect measurements, and measurement of ionic transport.[1]

The electronic semi-conductors can be divided into two classes. These are: reduction semi-conductors in which there is a deficiency of the electronegative element and oxidation semi-conductors in which there is an excess of the electronegative element. In the first case, the Hall constant is negative as it should be if the current carriers are negatively charged. Typical cases of reduction semi-conductors are zinc oxide whose properties have been extensively investigated by Fritsch, Baumbach, Wagner and others,[2–4] and titanium dioxide as was found in the experiments described in this paper.

The mechanism of electrical conduction in reduction semi-conductors can be explained in the following way. We can assume that the heated semi-conductor loses atoms of the electronegative element from the surface, leaving the electropositive element in excess. This type of conductivity is described by the relation

$$\sigma = kP_0^{-1/n}. \tag{1}$$

k and n are constants; P_0 = pressure of oxygen around sample; and σ = the conductivity.

These excess atoms which occupy interstitial positions can be thought of as providing additional levels from which electrons may be more easily released thermally into an allowed region for conduction.

In the case of oxidation semi-conductors, the sign of the Hall constant is positive, being opposite to that of the reduction semi-conductors. This would make it appear that the current in oxidation semi-conductors is carried by positive charges. This apparently anomalous behavior can be explained in the following way. We can assume that there is a band of quasi-continuous energy levels which are normally filled, thus preventing any net motion of electrons in either direction. If it is now assumed that there are additional levels lying a short distance above the filled band to which electrons may be excited and trapped, the conductivity can be explained by the motion of the vacancies thus produced in the previously filled band.

Semi-conductors are found to depend on the temperature according to the following equation.

$$\sigma = Ae^{-\epsilon/kT}, \tag{2}$$

where σ = the conductivity; ϵ = the activation energy for producing free electrons or free holes; T = the absolute temperature; k = Boltzmann's constant; and A = (const.) $\ln^{\frac{1}{2}} T^{\frac{1}{4}}$ ohm^{-1} cm^{-1} which is seen to be only very slightly dependent on the temperature and can thus be regarded as a constant.

Titanium dioxide is a white powder which finds extensive use today in the paint industry as a pigment as well as uses in the paper and textile industries. It exists in three allotropic forms: rutile, anatase and brookite. Rutile and anatase are the most common forms. Brookite is exceedingly rare, being very unstable.

Most of the work described in this paper was carried out on rutile, although some curves plotted from data taken on anatase are shown.

EXPERIMENTAL PROCEDURES

The samples used in these experiments were prepared by pressing 1.5 g of powdered titanium dioxide into cylindrical pellets ½″ in diameter and about ¼″ in length at a pressure of 36,000 lb./in.^{2}. These values in weight and pressure were chosen as standards after extensive experimenting because it was found that the pellets made under these conditions were of a convenient size and of a sufficient degree of durability. The density of the pellets thus made was about 50 percent of the single crystal density of the powder. By sintering these pellets for 10 hours at 1300°C in air their density became approximately 95 percent that of the single crystal.

The press used was made from a hydraulic truck jack capable of exerting a total force of eight tons. The die in which the powder was pressed was made of hardened tool steel equipped with two hardened plungers.

In making measurements on pressed powder samples it is very difficult to get results that are constants of the material being investigated. The results are greatly influenced by the pressure under which the samples are made, the amount

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[1] C. Tubandt, *Handbuch der Experimental Physik* (1932), Vol. 12, pp. 396–399.

[2] O. Fritsch, Ann. d. Physik **22**, 375 (1935).

[3] W. Schottky and C. Wagner, Zeits. f. physik. Chemie **11B**, 163 (1933).

[4] C. Wagner and H. H. von Baumbach, Zeits. f. physik. Chemie **22B**, 199 (1933).

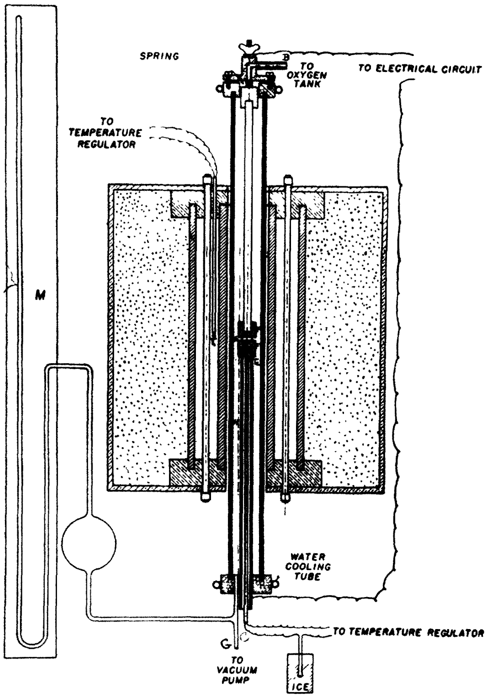

FIG. 1. Apparatus for measuring the electrical conductivity of titanium dioxide.

of sintering and the previous treatment of the sample. In making absolute measurements of a substance such as titanium dioxide it is obviously best to use a sample which has been sintered until it approaches as closely as possible the density of the single crystal. However, for making measurements in which diffusion plays an active part, such as the dependence of conductivity on oxygen pressure, it is found that much more valuable relative measurements could be obtained by using unsintered samples made under fixed conditions. It is undesirable to use highly sintered samples for this type of measurement because equilibrium is reached very slowly after a change has been made in the pressure of the vapor surrounding the sample.

This introduces a large uncertainty in the measurements because one can never be certain that the system has reached equilibrium, even after a long period of time. With the unsintered samples of approximately 50 percent single crystal density, reproducible results were obtained and the system apparently came to equilibrium within a few seconds after a change was made. This was indicated by the fact that the current through the sample very quickly reached a steady value, after a change in the pressure of the surrounding oxygen was made. With a well-sintered sample, the current drifted with time for hours or even days.

After considerable experimenting it was found that the best electrical contacts were metal films evaporated on the surface of the samples. The contacts in these experiments were made of gold evaporated on the parallel surfaces of the pellets. The samples before being placed in the vacuum chamber were carefully wrapped with aluminum foil to keep their sides free from gold.

In this work gold was found to have the following advantages over many other metals: (a) its melting point is sufficiently high (1063°C) so that it can be used at all temperatures at which these measurements were made; (b) its evaporation temperature (1445°C) is sufficiently low for easy evaporation; (c) it adheres readily to a clean tungsten filament by surface tension so that no crucible is necessary; and (d) it does not oxidize when heated in oxygen or in air.

The experimental equipment for making conductivity measurements at various pressures of the gas surrounding the sample and at various temperatures is shown in Fig. 1. The furnace proper consisted of two Alundum[5] tubes two inches and five inches in diameter and twelve inches in length, mounted concentrically. In the space between these tubes there were four

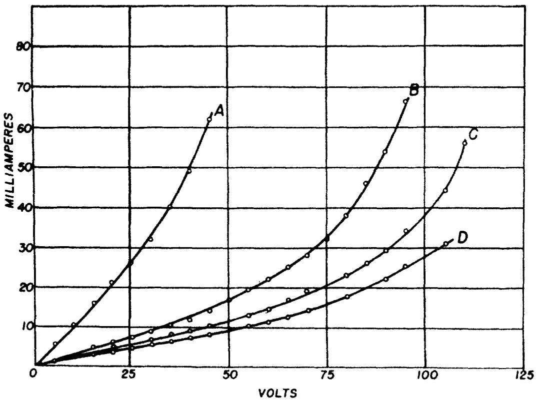

FIG. 2. Current as a function of voltage. A—2-mm mercury oxygen pressure; B—11.1-cm mercury oxygen pressure; C—38.8-cm mercury oxygen pressure; D—77.0-cm mercury oxygen pressure.

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[5] Alundum is aluminum oxide. Manufactured by the Norton Company.

Globar[6] heaters. The whole furnace was encased in a transite box approximately fourteen inches on each edge and packed with crushed firebrick for insulation. In order that the composition and pressure of the atmosphere surrounding the sample might be varied at high temperatures it was necessary that the samples be placed inside a quartz tube mounted in the furnace as shown in Fig. 1. The quartz tube was two feet long and one and one-quarter inches inside diameter and was fitted with grooved end plates waxed in place and cooled with running water to prevent the softening of the wax. The sample *S*, the parallel faces of which had been coated with gold by evaporation, was placed between the platinum electrodes *P*. These electrodes were held in place by Lavite blocks *F*, whose adjacent faces were machined plane to insure uniform contact over the surface of the pellet. The lower Lavite block was supported by a small quartz tube $\frac{5}{16}$ of an inch inside diameter which was closed at the upper end. The thermocouple T_2 used for measuring the temperature of the sample, was placed in the tube from outside the furnace. In this way the thermocouple could not come in contact with the strong oxidizing atmosphere surrounding the sample during many of the measurements, thus greatly increasing its life.

The platinum wires *H* connected the platinum electrodes to the brass end plates to which the external connections were made. However, it was found necessary to take the following precaution with regard to insulation. It was noticed that if the copper cooling tubes on the top and bottom end plates were directly connected with a rubber tube to complete the water circuit, some current was bypassed due to impurities in the cooling water. When fifteen feet of glass tubing was inserted in the cooling circuit between the upper and lower end plates, the current bypassed was negligible. *B* is a small tube used to admit the oxygen into the system. *G* is the tube used for evacuating the system. A closed end mercury manometer *M* was used for measuring the pressure of the vapor surrounding the sample. The thermocouple T_1 was used to control the temperature of the furnace. The thermocouple T_2 could not be used for this purpose because the time required for it to respond to changes in the temperature of the heating elements was great enough to allow the temperature to drift badly.

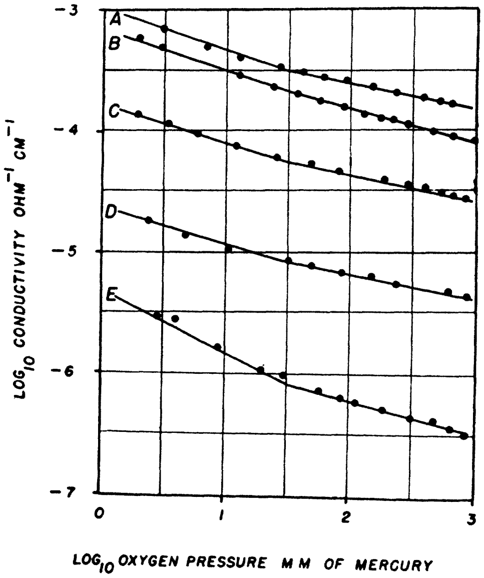

FIG. 3. Conductivity as a function of oxygen pressure. *A*—rutile, 968°C; *B*—rutile, 820°C; *C*—anatase, 861°C; *D*—rutile, 755°C; *E*—rutile, 626°C.

The conductivity was measured by the direct current fall of potential method. The advantage of this method is that it not only enables one to measure the conductivity but also to measure the current passing through the sample as a function of the voltage impressed on it. In this way one can determine to what extent Ohm's law is obeyed.

CURRENT AS A FUNCTION OF VOLTAGE

The curves in Fig. 2 show the current in milliamperes plotted as ordinate against the potential in volts plotted as abscissae. The data for each curve were taken with the pressure of the oxygen surrounding the sample maintained at a constant value. It is seen that for a short distance the variation is linear, which is as would be expected from Ohm's law. Beyond this point the curves deviate from a straight line, the current increasing more rapidly with voltage than Ohm's law predicts. In each curve it is seen that the deviation from linearity occurs when the power dissipated in the sample because

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[6] Globar heaters are made of silicon carbide. Manufactured by the Carborundum Company.

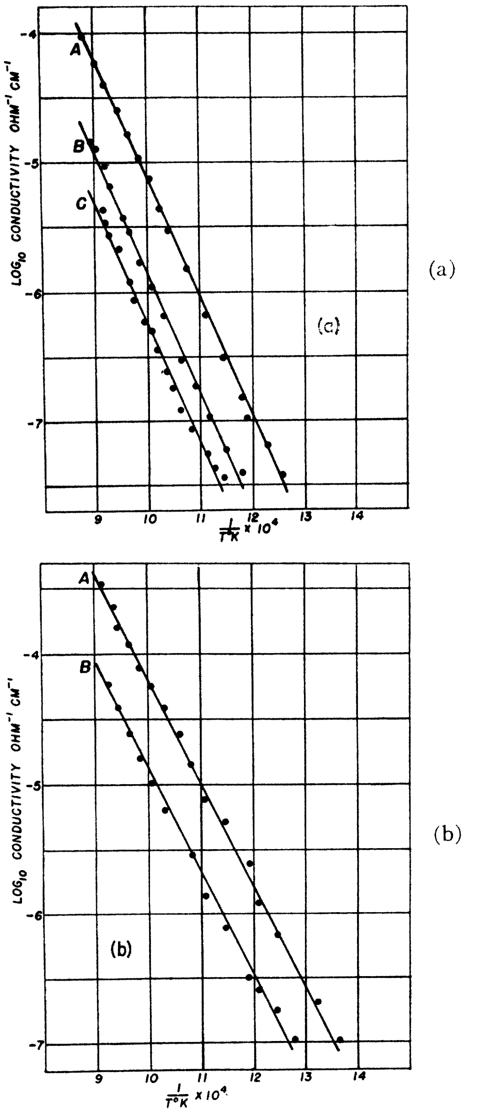

FIG. 4. Conductivity as a function of temperature. (a) Unsintered samples of rutile. *A*—0.1-mm mercury oxygen pressure; *B*—5-cm mercury oxygen pressure; *C*—79.5-cm mercury oxygen pressure. (b) Sintered samples of rutile. *A*—0.1-mm mercury oxygen pressure; *B*—14.0-cm mercury oxygen pressure.

of Joule heating is about 0.6 watt (0.95 watt/cm^3). When the Joule heating is less than this value the heat is dissipated fast enough so that the specimen reaches thermal equilibrium.

CONDUCTIVITY AS A FUNCTION OF OXYGEN PRESSURE

The dependence of the conductivity of rutile on the pressure of the surrounding oxygen is shown in Fig. 3. It is seen that for oxygen pressure above 30 mm Hg all the lines have a slope of approximately $-1/4.3$. The slope at pressures lower than this varies from $-\frac{1}{2}$ at the lower temperatures to $-\frac{1}{3}$ at the higher temperatures. If it is assumed that there is one free electron for each interstitial titanium atom the decomposition of the titanium dioxide can be represented by the reaction:

$$\mathrm{TiO_2 \rightarrow Ti^+ + O_2 + e^-}. \qquad (3)$$

With this assumption the slope of the lines at oxygen pressures above 30 mm Hg can be accounted for in the following manner.

Let n = number of interstitial Ti$^+$ ions or the number of free electrons, $N\mathrm{o}_2$ = number of O$_2$ molecules in gas surrounding sample ($N\mathrm{o}_2 \gg n$), N = possible number of sites for Ti$^+$ ions, ϵ energy required to create a Ti$^+$ ion, a free electron and one molecule of gaseous oxygen, A = the free energy; then

$$A = n\epsilon + kT\left\{ n\log\frac{n}{N} + n\log\frac{n}{C} + (N\mathrm{o}_2 + n)\log\frac{N\mathrm{o}_2+n}{C}\right\}. \qquad (4)$$

The first entropy term is that of the interstitial Ti$^+$ ions; the second entropy term is that of the free electrons, and the third is that of the oxygen vapor. If $N\mathrm{o}_2 \gg n$ the above can be written:

$$A = n\epsilon + kT\left\{ n\log\frac{n}{N} + n\log\frac{n}{C} + N\mathrm{o}_2\log\frac{N\mathrm{o}_2}{C}\right\}, \qquad (5)$$

$$\frac{dA}{dn} = \epsilon + kT\left\{ \log\frac{n}{N} + \log\frac{n}{C} + \log\frac{N\mathrm{o}_2}{C} + C_1\right\}$$
$$= \epsilon + kT\{\log n^2 N\mathrm{o}_2 + C_2\} = 0. \qquad (6)$$

The conductivity at a temperature T is

$$\sigma = Ae^{-\epsilon/kT} \qquad (7)$$

(where $A = 0.024\ \ln^{\frac{1}{2}} T^{\frac{1}{4}}$ ohm^{-1} cm^{-1}).

It is seen that the conductivity varies as $\sqrt{n}$ where n is the number of centers present (in this case the number of interstitial Ti$^+$ ions).

From Eq. (6) we have $n \propto N\mathrm{o}_2^{-\frac{1}{2}}$; replacing $\sqrt{n}$ by σ we obtain $\sigma \propto \sqrt{n} \propto N\mathrm{o}_2^{-\frac{1}{4}}$. This gives very good agreement with the curves to the right of the break in Fig. 3 whose slope is seen to be about $-1/4.3$.

The increased slope of the curves at pressures lower than 30 mm Hg is probably due to small impurities. The samples were as pure as could be conveniently obtained, but contained a number of impurities as the following chemical analysis shows:

TiO_2—98.5 percent
SiO_2— 1.09
P_2O_5— 0.27
MgO— 0.11 (approx.)
Fe_2O_3— 0.012.

CONDUCTIVITY AS A FUNCTION OF TEMPERATURE

Figure 4 shows the dependence of conductivity of the rutile form of titanium dioxide on temperature. The data of Fig. 4(a) were taken on unsintered samples whose bulk density was approximately 50 percent the single crystal density. The data of Fig. 4(b) were taken on well-sintered samples with a bulk density of 93 percent that of a single crystal. These data show that the law (Eq. (2)) $\sigma = Ae^{-\epsilon/kT}$ is well obeyed in the range of temperature investigated. The slope of these curves shows that the value of the activation energy (ϵ in the equation above) required to produce free conducting electrons was 1.75 electron volts for the unsintered samples and 1.7 electron volts for the sintered samples.

Figure 5 shows curves representing the conductivity of unsintered samples of rutile as a function of temperature at 10 mm and 300 mm of Hg, respectively. These curves were compiled from data obtained from Fig. 3. They should be very reliable in that they show the temperature dependence of the conductivity of rutile at a constant pressure for a number of different samples. They also indicate that the value of ϵ is approximately 1.7 electron volts. It is to be noted that the curve for 300 mm of Hg oxygen pressure was selected from the portion of the curves that can be explained by the theory outlined previously, whereas the curve for 10 mm of Hg oxygen pressure was selected from the anomalous portions of the curves where the slope is greater than theory would predict. The change in the slope of the curves of Fig. 3 is not sufficient to make any noticeable change in the activation energy as determined from the conductivity *versus* temperature curves. This shows that a very slight change in activation energy is sufficient to cause a deviation from proportionality, $n \propto N_{O_2}^{-\frac{1}{2}}$ derived from Eq. (6).

IONIC CONDUCTIVITY

The following method was used in an effort to detect the possible ionic conductivity of rutile. Three pellets which had been sintered in air for sixteen hours at 1250°C were polished on a flat plate until their parallel faces were plane. The samples were accurately weighed and placed in the furnace with these adjacent faces in good contact. A direct current which averaged 90 milliamperes was passed through the three samples in series for five days, which corresponds to a total charge of approximately 36,000 coulombs. The furnace was kept at 850°C during the experiment. The pellets were then removed and weighed again. The weights of the pellets before and after are recorded below:

	Before	After	Change
Top	1.4013 g	1.4008 g	−0.0005 g
Middle	1.4068 g	1.4066 g	−0.0002 g
Bottom	1.3965 g	1.3965 g	0.0000 g.

These data show that the upper limit of the change in weight due to a migration of ions cannot be greater than the experimental error involved in weighing. Since the charge passed through the samples was 0.37 faraday, it

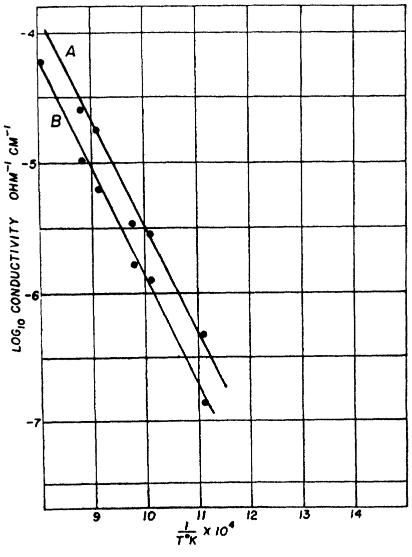

FIG. 5. Conductivity as a function of temperature. *A*—10-mm mercury oxygen pressure; *B*—30.0-cm mercury oxygen pressure.

seems conclusive that the ionic conductivity is negligible.

Inasmuch as the result of this experiment was negative, it was not necessary to employ the more elaborate means which enables one to separate the conductivities due to positive and negative ions which has been described by Tubandt.[1] One might raise the objection that the change in weight due to positive ions might exactly cancel that due to negative ions. This, however, would be extremely improbable in the case of titanium dioxide. The radius of the oxygen ion is 1.32A, while the radius of the titanium ion is 0.64A.[7] The titanium ions are therefore very much smaller and hence more mobile than the oxygen ions. As a result we should expect the positive ion transport number to be much greater than the negative ion transport number.

An attempt was made to determine the possible ionic conductivity by another method. This experiment was carried out in the following manner. A pressed strip of titanium dioxide 5 cm long and 8 mm wide was prepared and carefully balanced on the beam of an analytical balance above the knife edge. The position of the strip for balance was accurately marked by a small clip whose weight was exactly balanced by a similar one on the other side. This sample was then placed in the furnace and a charge of about 10,000 coulombs was passed through it. The sample was then accurately replaced on the beam of the balance and no change in weight could be detected. In the first method it is possible that the interfaces between separate pellets may be forming blocking layers which impede the free flow of ions. For this reason the second method was considered significant, because there are no boundaries of this type present.

HALL EFFECT MEASUREMENTS

The samples of rutile used for making Hall effect measurements were strips of pressed powder 5 cm long and 8×2 mm in cross section. As samples of titanium dioxide of these dimensions have a room temperature resistance of approximately 25×10^{12} ohms and since the equipment available could not make measurements at temperatures above 120°C, it would have been quite impossible to get a sufficiently high current density to detect a Hall e.m.f. For this reason it was necessary partially to reduce the samples to increase their conductivity by producing a deficiency of oxygen. The reduction was carried on in an atmosphere of hydrogen at a temperature of 500°C. By varying the time for reduction it was possible to bring the sample to any desired resistance. The best samples to use were those whose resistance was between 20,000 and 30,000 ohms. Gold was evaporated on the ends for making electrical contact. Near the center on opposite sides of the width were placed two small gold contacts for measuring the Hall e.m.f. Measurement of the Hall effect was very difficult, no well reproducible results being obtained.

The following equation was used to compute the Hall constant R:

$$R = -V/dIH, \tag{8}$$

where V = voltage developed in sample; d = thickness of sample; I = current; and H = field strength.

It was found that the Hall constant was of the order of magnitude of -10^{-7} volt/cm-amp.-gauss. This result is only qualitative at best. By assuming the value of the Hall constant to be -10^{-7} volt/cm-amp.-gauss the mean free path l for the conductive electrons is found to be approximately 5.1×10^{-7} cm. If R is known, the number of conducting electrons, n_f is found to be approximately $3.72\times 10^{9}/\mathrm{cm}^3$.[8]

These experiments are of value in that they indicate the order of magnitude of the mean free path and of the number of the conducting electrons. These Hall effect measurements do not rule out the possibility of ionic conductivity, but the transport measurements previously described show that the conductivity is almost entirely electronic.

In conclusion I would like to express my gratitude to Dr. Frederick Seitz and Dr. Park Miller for their helpful advice and criticisms, and to the Titanium Division of the Sherwin-Williams Company for part-time employment during the period in which this work was done.

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[7] W. H. Bragg, *Atomic Structure of Minerals* (Cornell University Press), p. 31.

[8] The equations for making these computations are:

$$R = -\frac{\pi e l}{(2\pi m k T)^{\frac{1}{2}}\sigma(Hz)} = -\frac{3\pi}{8}\frac{1}{n_f e C}.$$

See F. Seitz, *Modern Theory of Solids* (McGraw-Hill), p. 192.