Final Report - Contract Nonr 628(00)

THORIUM OXIDE RESEARCH

Bartol Research Foundation

FINAL REPORT

Contract NOnr 628(00)

Research on Electrical Conduction in, and Thermionic Emission from, Thorium Oxide and Similar Compounds

Contract Period: November 1, 1951 - January 31, 1954

Bartol Research Foundation
Whittier Place
Swarthmore, Pennsylvania

Office of Naval Research
Electronics Branch
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W. E. Danforth,	Assistant Director, Principal Investigator, (part time)
O. A. Weinreich,	Physicist, (full time)
Harry Bleecher,	Technician, (part time)

On April 1, 1953 O. A. Weinreich left the Bartol Foundation and assumed duties with the Tung-Sol Electric Corporation, Bloomfield, New Jersey. No work was done on the contract in the period between May 1, 1953 and September 30, 1953. On October 12, 1953, J. H. Bodine joined our organization, took up the work of this contract, and has been engaged with the Hall measurements and theoretical studies. D. L. Goldwater, whose primary responsibilities lie with the closely associated Contract NObsr-52592, has taken a significant part in the discussions relevant to this work. The present report was prepared by W. E. Danforth.

It is a pleasure to acknowledge the interest and support of Dr. W. F. G. Swann, Director of the Bartol Foundation.

I. ABSTRACT

1. General

Studies have been made of electrical and optical properties of homogeneous crystalline specimens of thorium oxide. The objective has been to obtain basic information pertinent to electron tube applications of this material. Definitive experimental data have been obtained regarding a wide range of topics. Theoretical interpretation is as yet incomplete. A brief statement of the results obtained follows.

2. Color Phenomena and Absorption Spectra

The relation of thorium oxide color to oxygen content and heat treatment has been established. Optical absorption measurements in the visible and ultraviolet have been made with specimens of crystalline material having different oxygen content. Coloring (and bleaching) by radiation, and coloring by passage of current, are described.

3. Electrical Conduction

Conductivity of thorium oxide crystalline specimens, as a function of temperature, has been studied in oxygen, hydrogen, nitrogen, helium and vacuum. Oxygen activates a relatively high value of conductivity.

4. Thermoelectric Effect

Seebeck effect of thorium oxide against platinum has been measured in different gases and oxygen. In oxygen, quantitative data were obtained which indicate p-type conduction. Slope of the

$\frac{dE}{dT}$ vs. $\frac{1}{T}$ plot agrees with the log σ vs. $\frac{1}{T}$ slope of the conductivity data.

5. Solubility of Hydrogen

Micro-gas-analysis apparatus was used to determine the solubility of hydrogen in thorium oxide. Results pertain to role of hydrogen in bleaching, and in lowering of the conductivity.

6. Rectifying Properties

The rectifying properties of the ThO_2-Pt contact were determined.

7. Dielectric Constant

Approximate measurement was made of the low frequency dielectric constant of thin plates cut from crystalline ThO_2.

8. Hall Effect

Measurements of Hall effect in crystalline ThO_2 at elevated temperatures were in progress at end of contract.

9. Theoretical Summary

The empirical data outlined above are discussed in relation to the simple energy band model with donors and acceptors. The ultraviolet cut-off gives an intrinsic energy gap of 3.9 volts. Oxygen-rich crystals show cut-off at 3.3 volts, suggesting a high density band of acceptors extending to .6 volts below the conduction band. With oxygen-poor crystals (intrinsic gap 3.9 volts) an absorption maximum at 3.1 volts points to a high density of donor centers at .8 volts above the filled band.

Conductivity vs. temperature in atmospheres other than oxygen yield a gap value of 2.4 volts to be compared with the 3.1 volt figure from optical absorption. Conductivity and Seebeck effect in oxygen both yield activation energies of .7 - .8 volts which would be interpreted as gap values of 1.4 - 1.6 volts, however, in this case, this interpretation requires further study on account of a presumed variation of density of impurity centers with temperature. Present lack of mobility data prevents accurate evaluation of impurity densities; using mobilities in copper oxide a value of 10^{18} is obtained for the non-oxygen case.

III. DESCRIPTION OF WORK

1. General

This contract was undertaken to provide basic information relative to thoria cathode research and development which has been in progress at the Bartol Foundation under Bureau of Ships Contract NObsr-52592.

The end-use of the information derived from both of these contracts is the development of improved electron-tube cathodes, thorium oxide being one of the more promising materials for heavy duty requirements of the kind met in the microwave field.

The types of cathode improvement for which information is being sought at Bartol are of two principal kinds: (a) increased electron emission at a given temperature, and (b) increased lifetime as a useful emitter. An understanding of electrical conduction in thorium oxide is pertinent to both of the above goals. The electronic energy level structure which is involved in electrical conduction is an essential part of the theory of electron emission. An understanding of ionic conduction in the material is basic to the life problem insofar as deterioration is due to electrolysis. The present contract is concerned with the electronic problems rather than the ionic, and, because of the basic role of conduction, a large fraction of the effort has been applied to electrical conduction rather than to thermionic emission.

The material used in these investigations was purchased in fused form from The Norton Company. Spectrographic arc analysis revealed aluminum and lanthanum as the principal impurities, both present to the order of magnitude 0.01 percent. Traces of chromium, copper, silicon, beryllium, tetanium, cerium, yttrium, and zirconium were also reported. Further description of the material and procedures for cutting and polishing crystalline specimens are given in a recent publication.[1]

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[1] W. E. Danforth, "Thorium Oxide and Electronics", Advances in Electronics, Vol. V, 1953 (Academic Press, Inc., New York, N. Y.)

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2. Color Phenomena and Absorption Spectra

Studies of the optical properties of a substance are basic to an understanding of its electrical behavior. Whenever an electrical property of thorium oxide is described, one must also state whether the data refer to the "high-oxygen" state or the "low-oxygen" state of the compound. A direct correlation has been found between oxygen content and color of a thorium oxide crystal.

The first clarification of the subject of thorium oxide color occurred at the Bartol Foundation during the beginning of the present contract. We quote from a previous publication.[1]

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[1] W. E. Danforth, loc. cit.

> ".....Recent studies at the Bartol Foundation have shown that thorium oxide may exist in red, colorless, or yellowish forms, depending upon heat treatment and oxygen content. A black form is also sometimes observed; but, so far, has been very little investigated.
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> " Experiments by Weinreich[2] showed that, generally speaking,

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[2] O. A. Weinreich and W. E. Danforth, Phys. Rev. 88, 953 (1952)

the red color of thorium oxide corresponds to the presence of excess oxygen; a crystal heated in oxygen at 1000° C, say, will invariably be red. This condition is denoted as 'oxygen-red'.

" If an oxygen-red crystal is heated (again, say, at 1000° C) in hydrogen or vacuum, the color disappears completely (no measurable change of weight). This colorless form is, for brevity, called 'white'.

" If a white crystal is exposed to ultraviolet radiation (sunlight will do) at room temperature, a red color is produced which, to the eye, is indistinguishable from the oxygen-red condition. This condition is called 'radiation-red' and differs from oxygen-red by, for one thing, the fact that radiation-red will bleach immediately to white at 200° C, whereas oxygen-red will not.

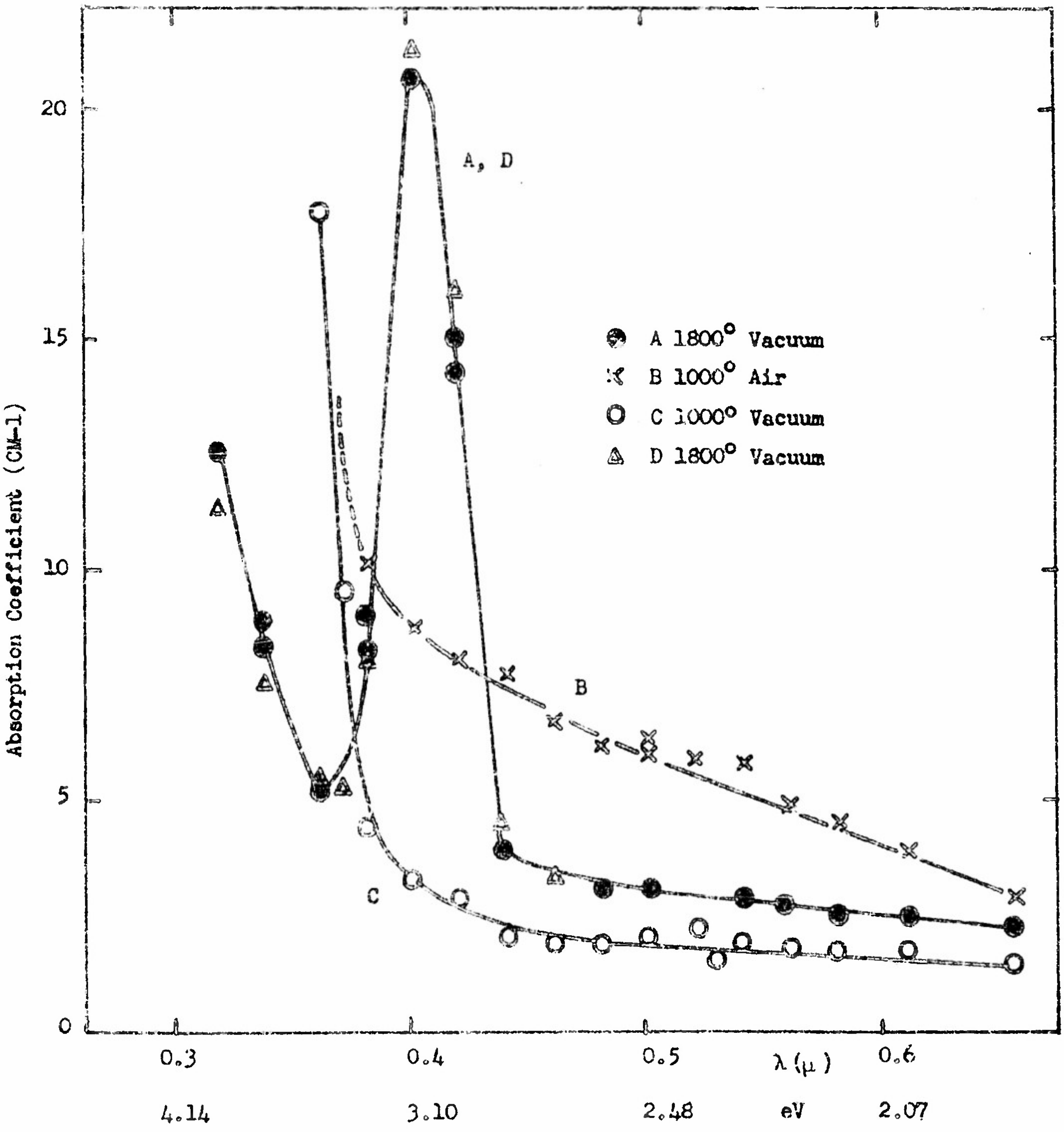
" Further optical changes take place when the material is subjected to higher temperatures. If a crystal in either the white or red condition is vacuum-fired at 1800° C, it assumes a yellowish color. Also a measurable loss of weight of the order of 10^{-3} percent is found. Spectroscopically, it is found that the short-wave limit of transmission is shifted from 3700 Å to 3200 Å and that an absorption maximum appears at 4000 Å. Absorption data taken by Weinreich with a double quartz monochromator and photomultiplier are shown in Fig. 1. To show the reproducibility of the data, the material has been carried through the following cyclical treatment: (a) heating to 1800° C in vacuum, (b) heating to 1000° C in air, (c) heating to 1000° C in vacuum, and (d) reheating to 1800° C in vacuum.

" The solid circles show the absorption curve which is obtained after process (a). One notes the bell-shaped maximum at 4000° Å. Process (b) heating in air, causes absorption of oxygen and pronounced change of spectrum as shown by the crosses. The bell-shaped absorption has disappeared, and the cut-off has shifted to longer wave-lengths. The crystal, if now examined cold, will be a deep red color. Process (c) bleaches the crystal to clear white with no measurable weight loss. The absorption is now shown by the open circles. Process (d) heating again to 1800° C in vacuum, brings the crystal back to the condition following process (a) and gives the results shown by the triangles. Agreement between the triangles and solid circles shows that the crystal has been brought back to its original state."

Briefly, and empirically speaking, thorium oxide may be said to be in one or the other of two states, (a) the high-oxygen state, and (b) the low-oxygen state. In the high-oxygen state, the crystals are either red or colorless; in the low-oxygen state they are yellow.

The correspondence of these two "states" with theoretical descriptions of the material has not yet been made. It is possible

Fig. 1. Optical Absorption in Thorium Oxide



that, as the theoretical picture develops, the high-or-low oxygen classification will be found without precise meaning and may be set aside. Until then we will use it as a working guide.

Fig. 2 shows the relative change of spectral absorption in the visible when a white high-oxygen crystal is reddened by radiation. The measurements were taken with a double quartz monochromator and photomultiplier. To eliminate errors due to variations of light intensity, etc., only a portion of the specimen was exposed to radiation; the other part of the crystal remained colorless and served as a control. Each point on the graph was obtained by the following process. A reading of transmitted light intensity was made with the light traversing the colorless portion, (position 1.) The crystal is then shifted so that the light traverses the red portion, (position 2.). The ordinate of a point on the curve is then the ratio of the reading for position 2 to that for position 1. The upper curve gives the data before irradiation of the crystal; the departures from 100 percent can be accounted for by experimental error and non-uniformity of the specimen.

One notes a maximum of absorption for the red crystal in the neighborhood of 4000 Å. It is still an open question whether this bears any relation to the maximum which is shown by a low-oxygen crystal in the same region.

Regarding the shift of ultraviolet spectrum when a high-oxygen crystal is converted to the low-oxygen form by vacuum firing, the question may be asked: Which of these absorption spectra are to be regarded as the intrinsic absorption of the stoichiometric ThO_2 crystal? Or are both, perhaps, intrinsic, the change being one of

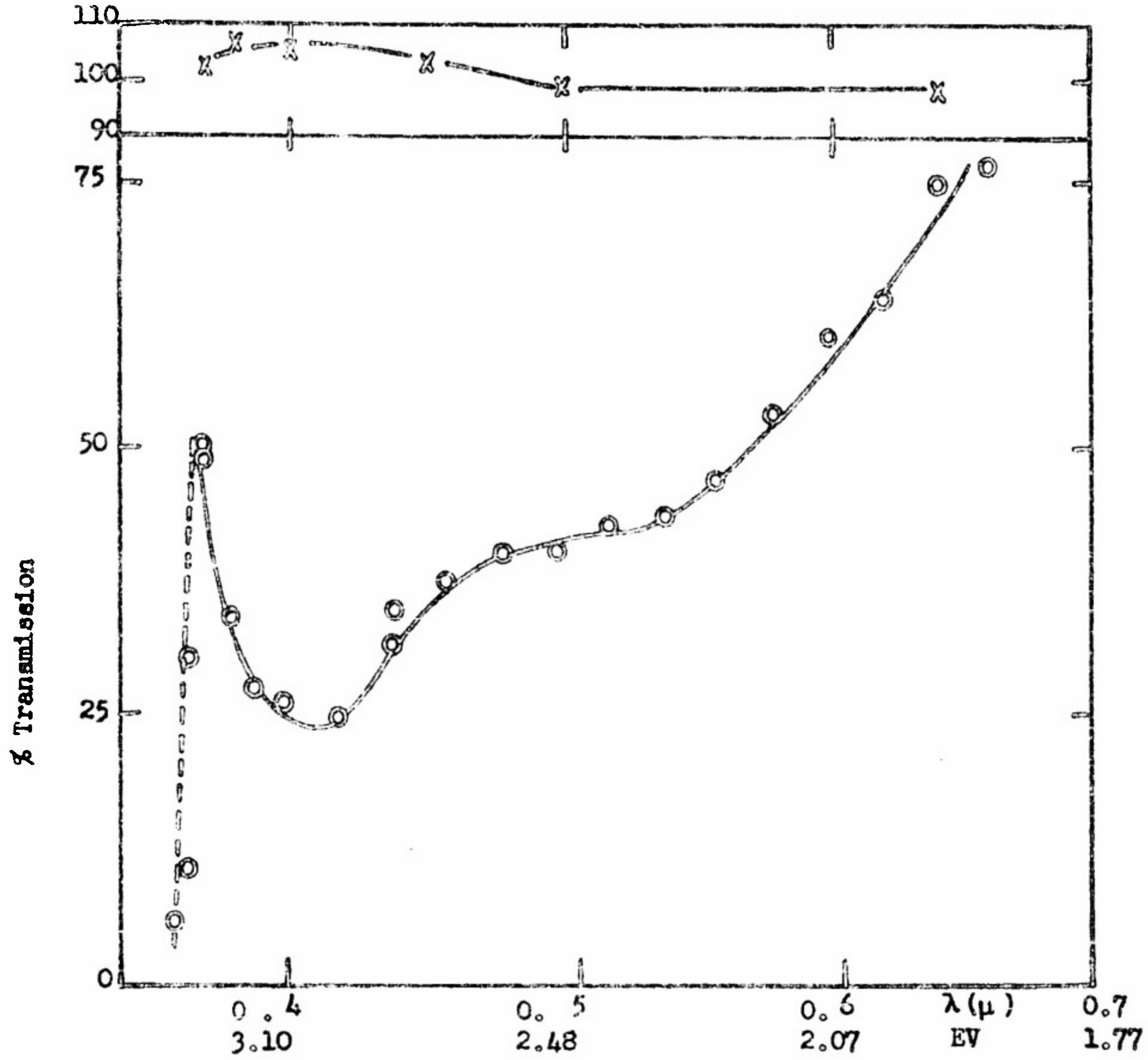


Fig. 2. Spectral effect of Radiation Reddening

crystal structure?

It would seem that the last named hypothesis might be ruled out at once. If the change from the "white" form to the "yellow" form is a change of intrinsic crystal structure, one would expect that, with sufficiently slow cooling, the transition back to the "white" form would take place, reabsorption of oxygen being unnecessary. No such change has been observed; absorption of oxygen appears essential to the shift of spectrum. X-ray observations have confirmed that no change of structure accompanies the change from white to yellow.

If it is assumed that one of these forms is the stoichiometric composition, it is more probable that this would be the low oxygen state. To hypothesize that the high-oxygen state is intrinsic means that the low-oxygen state is the result of thermal decomposition; this is improbable on thermochemical grounds.

The amount of oxygen involved, of the order of 10^{17} - 10^{18} atoms/cc, appears sufficient to account for the high absorption coefficient encountered between 3700 and 3200 Å and attributed, on this hypothesis, to the presence of excess oxygen.

The amount of oxygen involved in the change of red to white is undetectable by weighing and would therefore appear to be of the order of 10^{16} atoms/cc or less.

It has already been stated that the oxygen red crystal will bleach in vacuum at 1000° C. This bleaching is found, as would be expected, to take place in any oxygen-free atmosphere such as hydrogen, nitrogen, or helium. The dependence of this bleaching on temperature has not been thoroughly investigated; it has been observed to take place readily at 700° C but not in any reasonable time at 200° C. No bleaching of the oxygen-red crystal by radiation has been observed.

As already stated, a white high-oxygen crystal will redden when exposed to ultraviolet radiation. The bleaching of this radiation-reddening has been accomplished in two ways. It has been found that, regardless of the atmosphere, radiation-reddening will disappear when the crystal is heated to 200° C. The red color may also be destroyed by exposure to visible light of wave-lengths greater than 4100 Å. More precise determination of the wavelengths involved would be desirable.

Since a white crystal will convert to red by the addition of one part per million or less of oxygen, it would be expected that this phenomenon might be used for the detection of oxygen produced by electrolysis when a current is passed through a white crystal. This is indeed the case; some results in this connection are included in the next section.

3. Electrical Conduction

A. Tube for simultaneous determinations of conductivity and thermionic emission.

Before the beginning of this contract, work had commenced on a rather ambitious tube for this purpose. It is shown schematically on Fig. 3. The tube consists of a small vacuum furnace for raising a crystalline specimen to the desired temperature. A molybdenum anode, at the same temperature as the cathode, was intended to provide measurement of thermionic emission. At the same time the conductivity of the specimen could be determined with null probes.

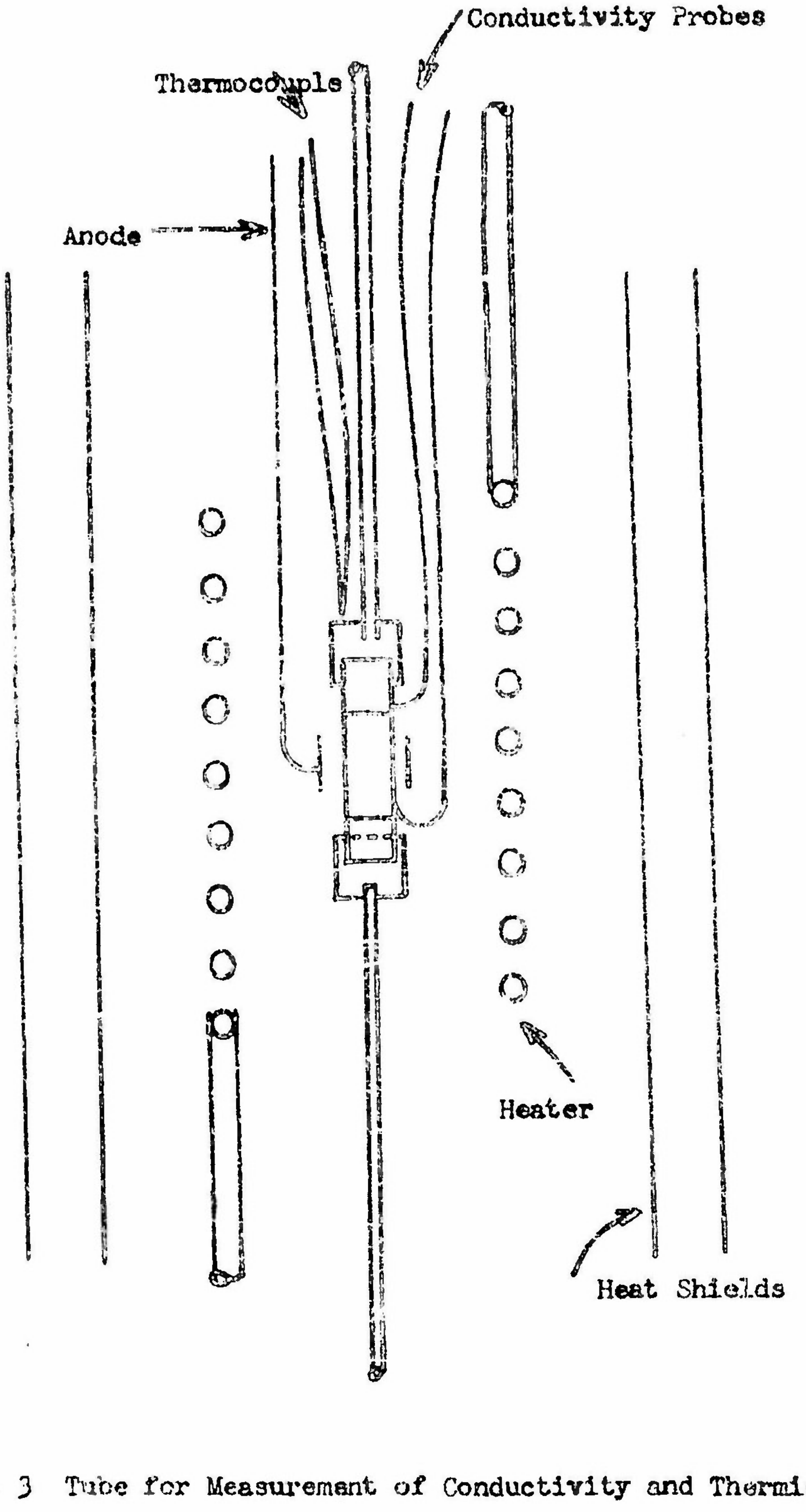


Fig. 3 Tube for Measurement of Conductivity and Thermionic Emission

A thermocouple was included for temperature measurement.

One of these tubes was completed, and preliminary work was carried out with it during the first few months of the contract. The technical difficulties were considerable. The current voltage relation of the anode had to be studied and correctly interpreted in order to yield a value of field-free emission; the fine wire probes tended to open circuit and when this occurred, it was necessary to disassemble the tube. However, the experiment appeared to be feasible.

This study was, nevertheless, discontinued before final results were achieved. This was not primarily because of difficulties but was based rather on logical considerations. When the experiment was first conceived, we were unaware of the magnitude of electrolytic effects in single crystals; the existence of these effects, the awareness that large and variable amounts of free thorium are likely to be present in the crystal and/or on its surface make the interpretation of the experiment difficult. These considerations, plus the fact that the experiment was proving to be time-consuming, made it seem more advisable to proceed with other and somewhat less elegant types of conductivity studies. It may be advisable to return to this experiment at a future time.

B. Previous Conductivity Studies

A review of this matter is given in reference 1. All previous quantitative studies were conducted on sintered material and the conductivity in vacuum has been found to be markedly dependent upon the history of the specimen as regards passage of current. This would be expected in view of the presence of electrolysis. In the studies of Danforth and Morgan,[3] measurements were made on sintered specimens, provided with potential probes, and mounted in a vacuum furnace. Pulsed measurements of conductivity were made as a function of temperature for several states of activation by current. Activation energies between 3.2 and .58 volts were found. Values of conductivity as low as 1 ohm-cm at 1027° C and 10 ohm-cm at 727° C were found after subjecting the specimen to direct current of 7.6 A/cm^2. The different states of activation, when related to the simple semi-conductor model, showed variation of activation energy alone, the density of impurity centers remaining more or less constant.

A preliminary experiment[4] concerning conduction in a homogeneous crystal of thorium oxide was carried out at Bartol in the fall of 1951. It was observed that electrolytic phenomena were very pronounced when charge amounting to a few coulombs was passed through a thoria crystal in vacuum at 1300° C. The first effect is a blackening of the interior of the crystal; this is followed by the formation of a metal coating on the surface.

Such phenomena made it evident, as stated earlier, that the study of conductivity in thorium oxide is a subject of greater empirical complexity than was first thought. It was realized that the conduction of electricity in thorium oxide as used in practice, e.g. in cathode coatings, is a very different matter from that

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[3] W. E. Danforth and F. H. Morgan, Phys. Rev. 79, 142 (1950).

[4] W. E. Danforth, Phys. Rev. 86, 416 (1952)

conduction which takes place in an unelectrolyzed thorium oxide crystal. Conduction in an actual cathode coating is intimately bound up with the presence of a considerable amount of free metal. It is, in fact, the presence of this free metal, produced by electrolysis, which so increases the electronic conduction of a cathode coating as to reduce the rate of electrolysis to a point where the cathode has a reasonable useful life.

Work on single crystals is obviously essential to the understanding of the cathode coating, but it became apparent that an understanding of the coating would not be immediately given when an understanding of the crystal was attained. Complete knowledge of single crystal behavior provides means by which, through much additional thought and experiment, knowledge of the coating behavior can be reached.

C. Studies in Gas Atmospheres

Various objectives are involved in the carrying out of studies in different gas atmospheres. Oxygen is of obvious interest regarding the question of the existence of p-type conduction produced, for example, by thorium vacancies. A more immediate reason for using an oxygen atmosphere is the desirability of working with a system which is stable in time. As already stated, a thoria crystal in vacuum acquires, in a short time, a metallic coating when current is passed through it. Only a short time is available for that kind of observation which might be said to relate to the thorium oxide structure itself. By doing the experiment in an oxygen atmosphere, a relatively stable situation is created.

The results to be described were obtained with rectangular specimens somewhat less than 1 cm on an edge. Since an oxygen atmosphere was to be used, molybdenum could not be used as an electrode material and platinum was used. Coatings of platinum were evaporated on opposite faces of the parallelepipeds; connection to the coated faces was effected with flat platinum contactors held in place by pressure. Conductivity values quoted were obtained from current and voltage values with these specimens. The question might be raised, since potential probes were not used, whether the results might not be affected by interface phenomena. The method chosen had the advantage of greater ease of performance, was more economical of the rather expensive fused material, and, if proved valid, would lend itself more easily to determination along different crystal directions. Before accepting the method as valid, however, an experiment was performed to investigate this point. A cylindrical specimen was prepared with platinum coatings on the ends and potential probes as well. Resistance determinations by null measurements on the probes were compared with those obtained by the simple current-voltage method and no significant differences were found.

The temperature determinations in these studies were made with Pt ⟶ Pt-Rh thermocouples spotwelded to the platinum contactors. A schematic diagram of the measurement apparatus is shown in Fig. 4. The temperature range is between 650° and 1000° centigrade. As described in the caption to that figure, the measurement was of "pulsed" character in order to avoid the time effects which occur when current is drawn continuously.

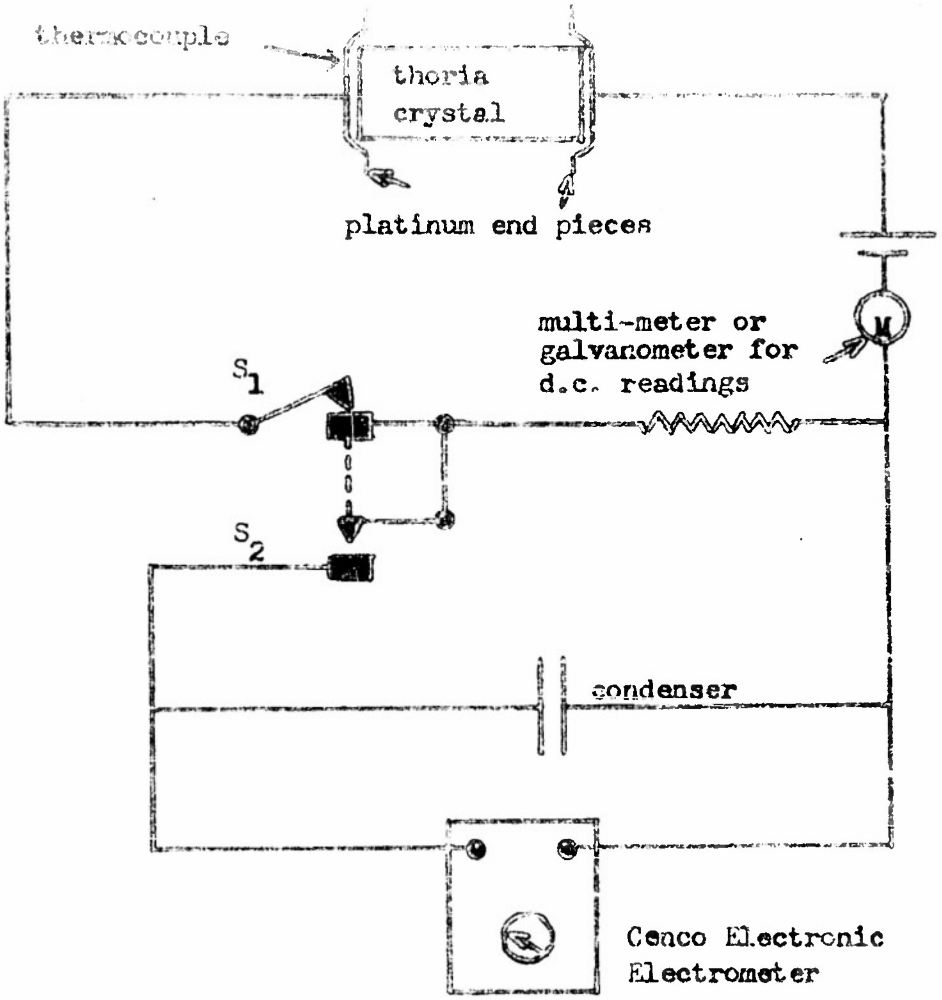


Fig. 4. Schematic Representation of Experimental Arrangement.

The thermocouple is connected to a Leeds & Northrup Type K Potentiometer.

The mechanical linkage between S_1 and S_2 is such that both may be closed by pressing S_1; and after both are closed, if the pressure is released, S_2 must open first. When both are closed, current starts to flow through the crystal and the condenser starts to charge. After the condenser-resistor combination has reached equilibrium, the switches are opened, and since S_2 opens first, the voltage on the condenser represents the current which was flowing. The time constant of the isolated condenser-electrometer circuit is so long that the reading may be made for many seconds after S_2 is opened. The arrangement has been worked out in practice so that the whole cycle above described is performed by tapping S_1 momentarily, and a current reading may be obtained while passing only a small total charge through the crystal.

The results of the measurements are given in Fig. 5 in which log of conductivity is plotted against reciprocal temperature. The lower curve in this diagram shows results obtained in an atmosphere of hydrogen or helium. They were made on different crystals. Measurements taken in vacuum on a third crystal lie somewhat below this line but still fairly close to it.

It seems, therefore, that the conduction in the absence of oxygen is not markedly dependent upon the atmosphere.

The addition of oxygen, however, increases the conductivity by a factor of the order of 10. In the high temperature region the results are nicely reproducible; values taken with a dozen crystals agree within about 10 percent. A break of slope occurs at about 1000° K and at lower temperatures the measurements become progressively more difficult on account of the time required for the system to come to equilibrium.

The time required for the conductivity to reach a new equilibrium when the atmosphere is changed from oxygen to non-oxygen, or vice-versa, is quite rapid at temperatures around 1100° C; the new value is attained in a few seconds. In the 700° K region the time required will be many minutes. Quantitative consideration of these time-phenomena in terms of probable diffusion coefficients remains to be done.

Application of semi-conductor theory to these data would require mobility data which are not available. Using mobility values for copper oxide, however, density of impurity centers is of the order of 10^{16}. This is based upon the slope of the high temperature portion of the oxygen curve.

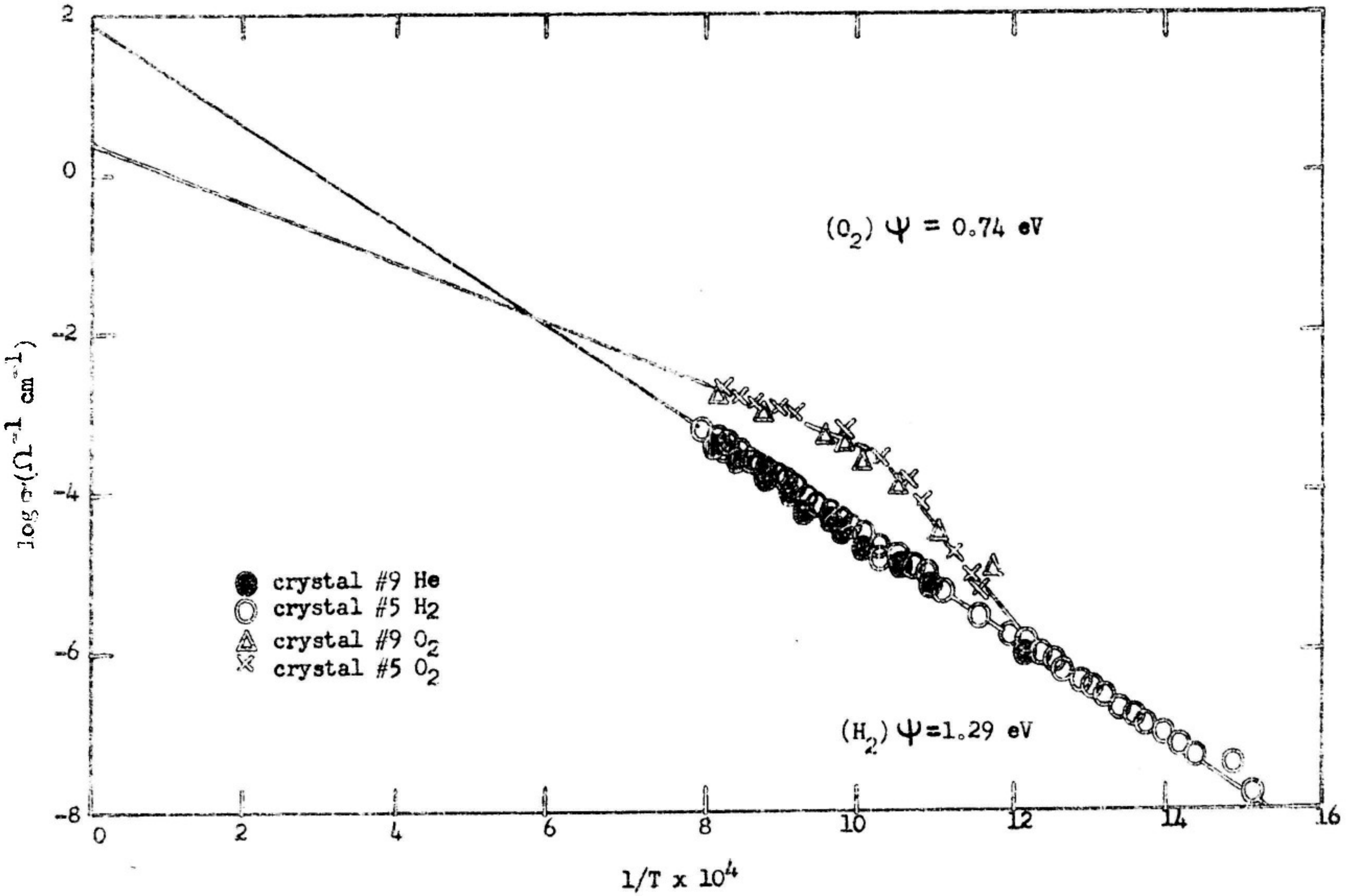


Fig. 5. Effect of Oxygen Content upon Conductivity

A similar calculation carried out for the non-oxygen curve will involve a higher value of the energy gap, and, accordingly, a higher density of centers of the order 10^{18}.

As stated earlier, the conductivity values from crystal to crystal show fair reproducibility, of the order of 10 percent. Values of slope, however, show a scatter also of the order of 10 percent and this is, of course, reflected in a high degree of uncertainty in the calculated density of impurity centers.

The elementary semi-conductor theory postulates a density of centers which is independent of temperature. In the case of a solid immersed in an atmosphere of a gas whose nature is pertinent to the activation, this assumption is doubtful to say the least.

In the case of the non-oxygen curve, the similarity of data when using hydrogen or helium or vacuum indicates that neither hydrogen or helium have a part in the creation of impurity centers and the calculated value of this quantity probably has some meaning when oxygen is not present.

With an oxygen atmosphere, however, it appears that dissolved oxygen must play an essential role in the conductivity mechanism. It seems certain, therefore, that, for this case, a calculation of the density of centers, based upon the assumption that this quantity is independent of temperature, is quite meaningless.

In this connection, we have carried out measurements of the dependence of conductivity upon oxygen pressure. Some data regarding this are shown in Fig. 6.

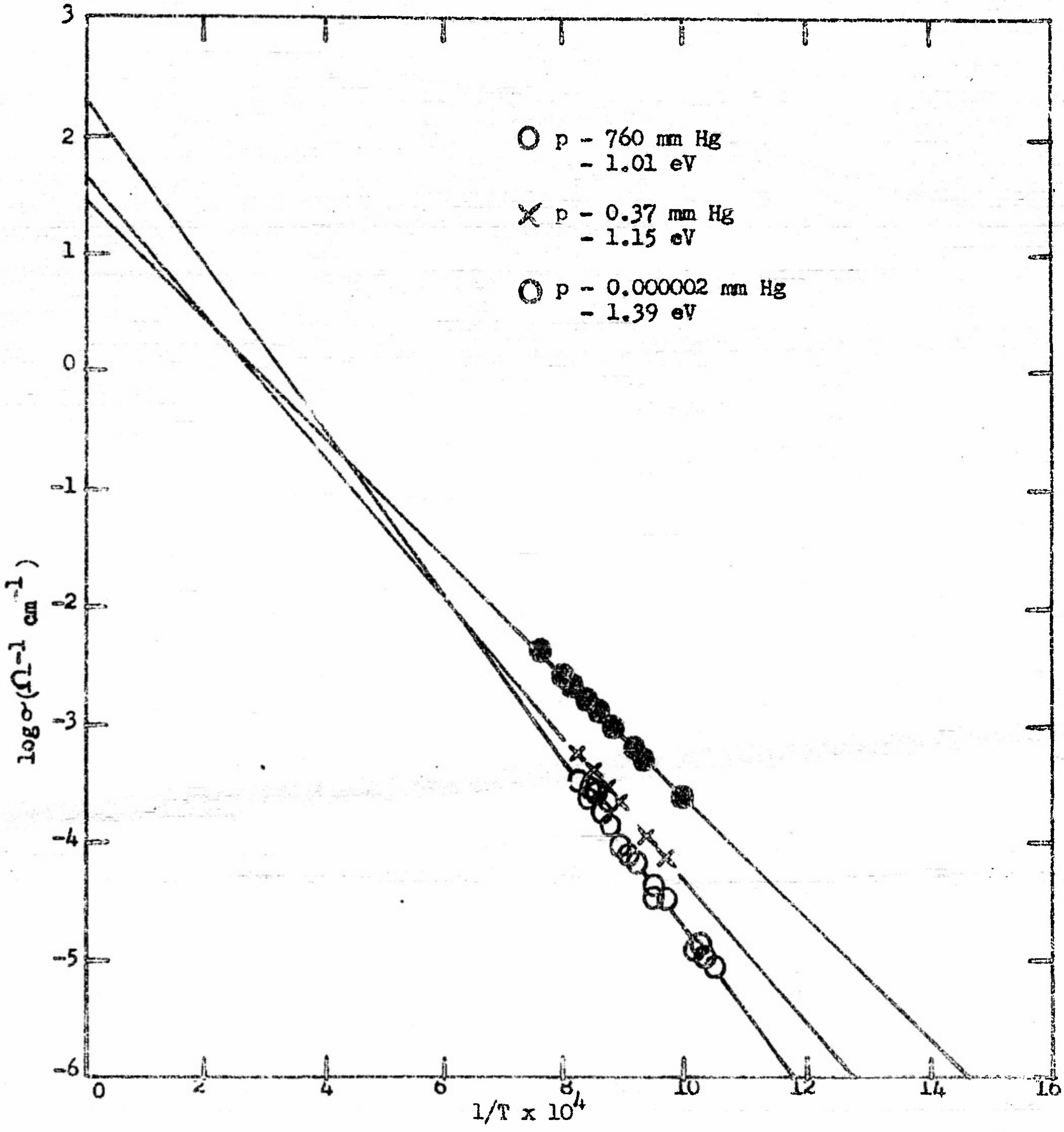


Fig. 6. Dependence of Conductivity upon Oxygen Pressure

The lowest curve shows data taken in vacuum. The two upper curves correspond to two different pressures of oxygen surrounding the specimen. Non-conformity to the elementary theory is immediately evident from the fact that the intercept, and accordingly the density of centers which would be computed, is a decreasing function of the oxygen pressure.

The functional relation between conductivity and pressure is sometimes derived by considering an equilibrium reaction equation, involving charge carriers, vacancies, etc., and applying the law of mass action. If we assume that we are dealing with p-type conduction involving vacancies produced by the removal of quadruply-ionized thorium, we arrive at a pressure-to-the-1/5th-power law. Fig. 7 shows data regarding this functional relation. We see that the experimental exponents are somewhat smaller than 1/5th.

Although there is no visible evidence of electrolysis in a thorium oxide crystal in an oxygen atmosphere, the passage of current has a pronounced effect upon the conductivity of the specimen. Since the passage of current does not produce a temperature rise which can account for the change of conductivity, the existence of such time changes points to ionic migration of some kind. Fig. 8 shows two curves of current through a specimen as a function of time, the specimen being held at constant voltage. It is seen that, as might be expected, the equilibrium is attained in much shorter time at the higher temperature. It is also seen that the relative increase of conductivity is a factor of more than 10 at the lower temperature (580° C) and a factor of only about 3 at the higher temperature (675° C). Presumably the increase is caused by an increase of oxygen content as a result of electrolysis. The lower

Fig. 7. Functional Relation Between Conductivity and O_2 Pressure

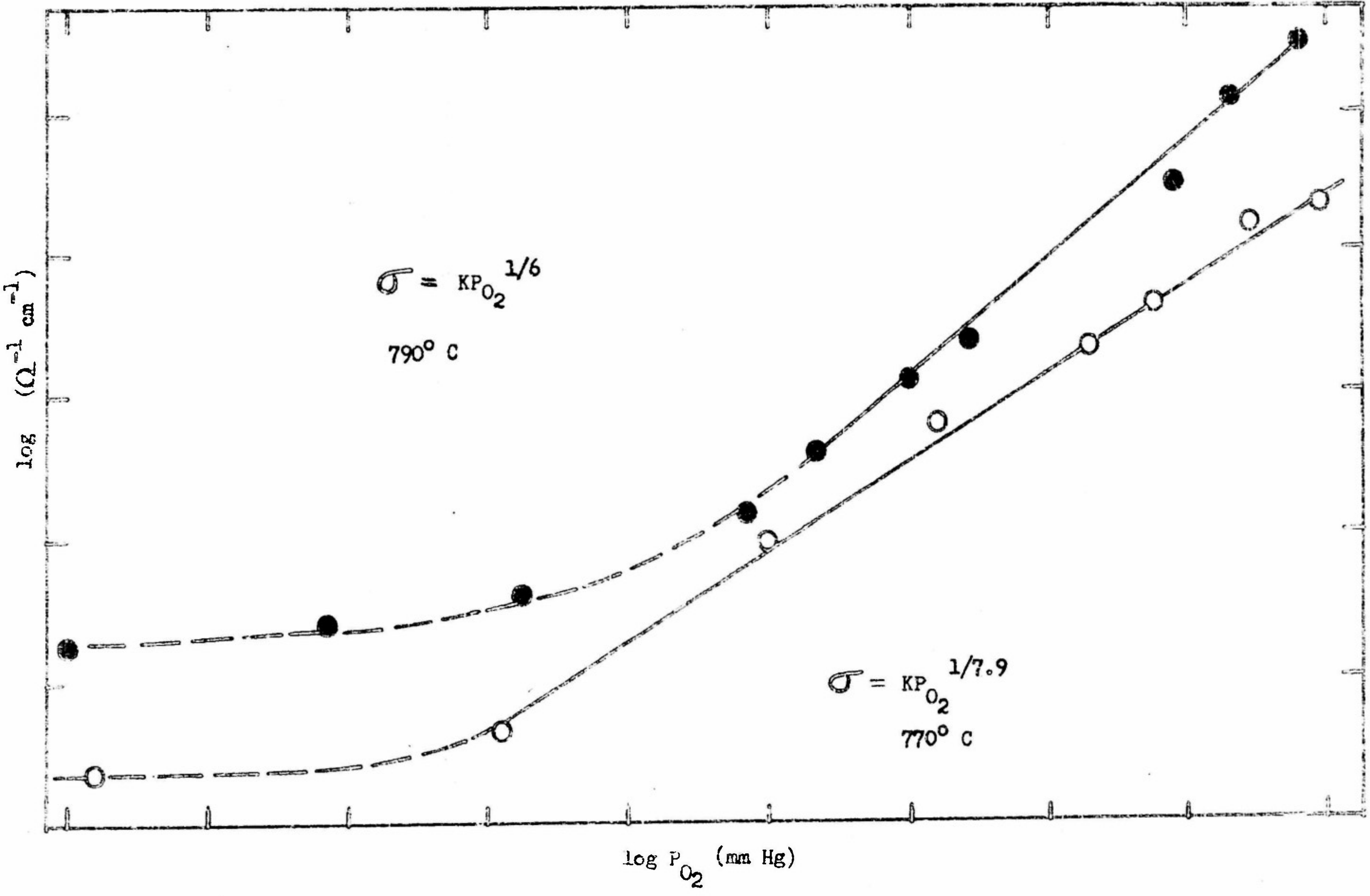
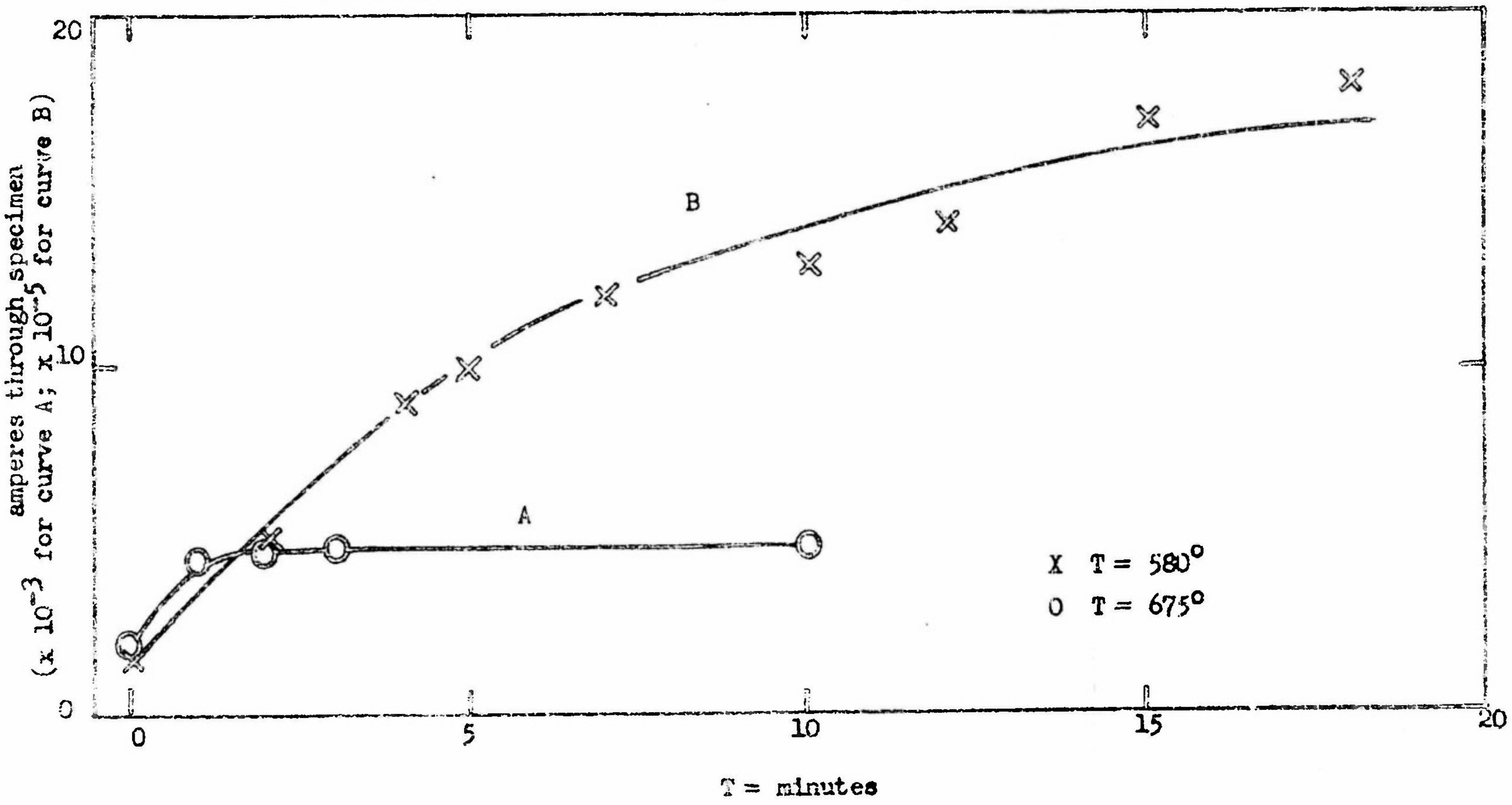


Fig. 8. Conductivity of thoria in oxygen at two temperatures. Current was passed continuously during each run. The ordinate is given in terms of current; since this current was passed at constant voltage, the ordinate scale may be considered to be conductivity in arbitrary units.



factor of increase at the higher temperature could be due to a greater preponderance of electronic conductivity at that temperature.

When current is passed continuously through a thoria crystal heated in hydrogen, the initial rate of change of conductivity is much less than in other atmospheres. If the atmosphere is changed from hydrogen to helium, a conductivity increase of two orders of magnitude occurs at 680° when current is passed continuously. This is shown in the latter part of Fig. 9.

It has been noted that the conductivity change and color change occur simultaneously when the atmosphere in which the thoria crystal is being heated is changed from oxygen to hydrogen. Results concerning this type of change are shown in part in Fig. 9. It is important to note the method whereby the color was ascertained at a particular stage of the experiment. The conductivity measurements are made, of course, with the crystal at the temperature noted on the curve, and the desired gas flowing around it. If the color is to be ascertained, the crystal on its supporting structure is drawn out to a cool section which extends outside the furnace. After about one minute, the crystal will be cool enough for its color to be noted. It is then returned to the hot area and conductivity measurements resumed. By color, then, is meant that color which is observed when the crystal is cooled rather rapidly in the atmosphere in which it has been heated.

Referring again to Fig. 9, it is seen that the conductivity change in helium was not accompanied by complete bleaching from the original red color which was present in oxygen. This observation was not conclusive since it is obvious from the figure that the

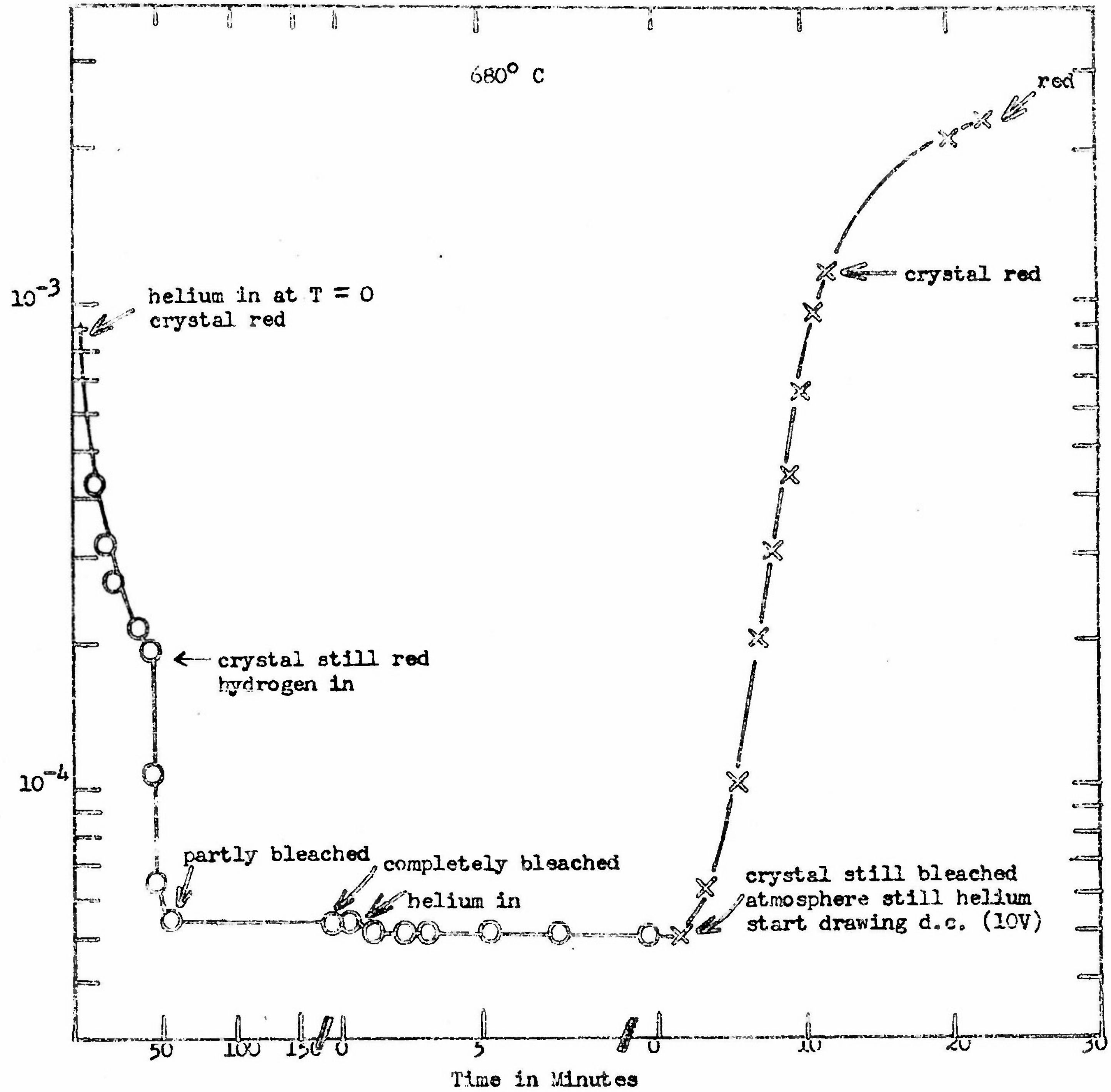


Fig. 9. Changes of Color and Conductivity

conductivity change had not gone to completion. On admitting hydrogen, simultaneous rapid bleaching and drop of conductivity were observed. At the conclusion of this process, the atmosphere was again changed back to helium with no effect on the conductivity (observed by the pulsed method) or on the color. Now the large conductivity change due to current drawing in helium (as previously described) was produced, and this was found to be accompanied by a return to the original red coloration. The rapidity of this change is strongly dependent upon the current density.

It has been stated that if the crystal was held in hydrogen, and the conductivity measured by infrequent short pulses, no conductivity or color changes occurred, the crystal being bleached and the conductivity low. If current was passed continuously when the thorium crystal was heated in hydrogen, a blackening of the crystal took place, appearing first at the cathode end of the crystal and spreading out toward the anode, so that finally the whole crystal was black. The blackening progressed at the rate of about 3 mm for each coulomb passed through the crystal. If the current was reversed after the crystal was blackened part way across, the first blackened region would appear to recede toward the new anode, while a new region of blackness would appear at the new cathode. Thus it is supposed that the blackening is associated with the migration of positive carriers, either metal ions or oxygen vacancies. The blackening produced could not be bleached out by heating the crystal in vacuum or in inert gas or in hydrogen. It could be partly removed by heating the crystal in oxygen, but even this treatment would not restore the specimen to its original optical clarity; cloudiness and irregular dark areas would still be present.

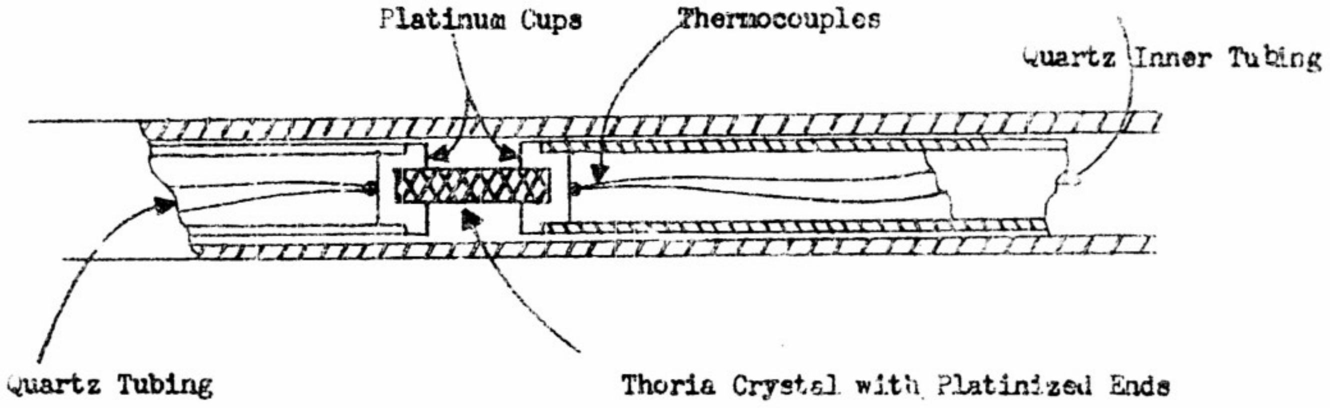
4. Thermoelectric Effect

Investigations of the Seebeck effect in thorium oxide were undertaken primarily to provide additional data relative to sign of carriers and to determination of energy gap values.

An attempt was made to study the Seebeck effect in vacuum at temperatures near the operating region (1300° - 1600° C). Results were not regarded as conclusive and, pending further work, the data were not reported. Large thermal EMFs were observed (e.g. .5 or more mm/degree) but time effects were prominent.

An investigation was completed, however, of Seebeck effect in an oxygen atmosphere. Fig. 10 shows the apparatus with which these measurements were carried out at atmospheric pressure. The specimen is shown held by spring pressure between platinum cups to which are spotwelded the noble metal thermocouples. This assembly is enclosed in a fused quartz tube through which the desired gas could be permitted to flow.

The means of raising the specimen to the desired temperature and of creating the temperature gradient are not shown in the figure. A split stainless steel cylinder, having an internal bore to accommodate the quartz tube, was fitted about the tube and raised to incandescent temperature by means of a circular gas burner. If the sleeve were placed symmetrically with respect to the specimen, the temperature of the specimen would be uniform; displacing the sleeve towards one end or the other would create the desired gradient.



Platinum Cups
Thermocouples
Quartz Inner Tubing
Quartz Tubing
Thoria Crystal with Platinized Ends

Fig. 10.

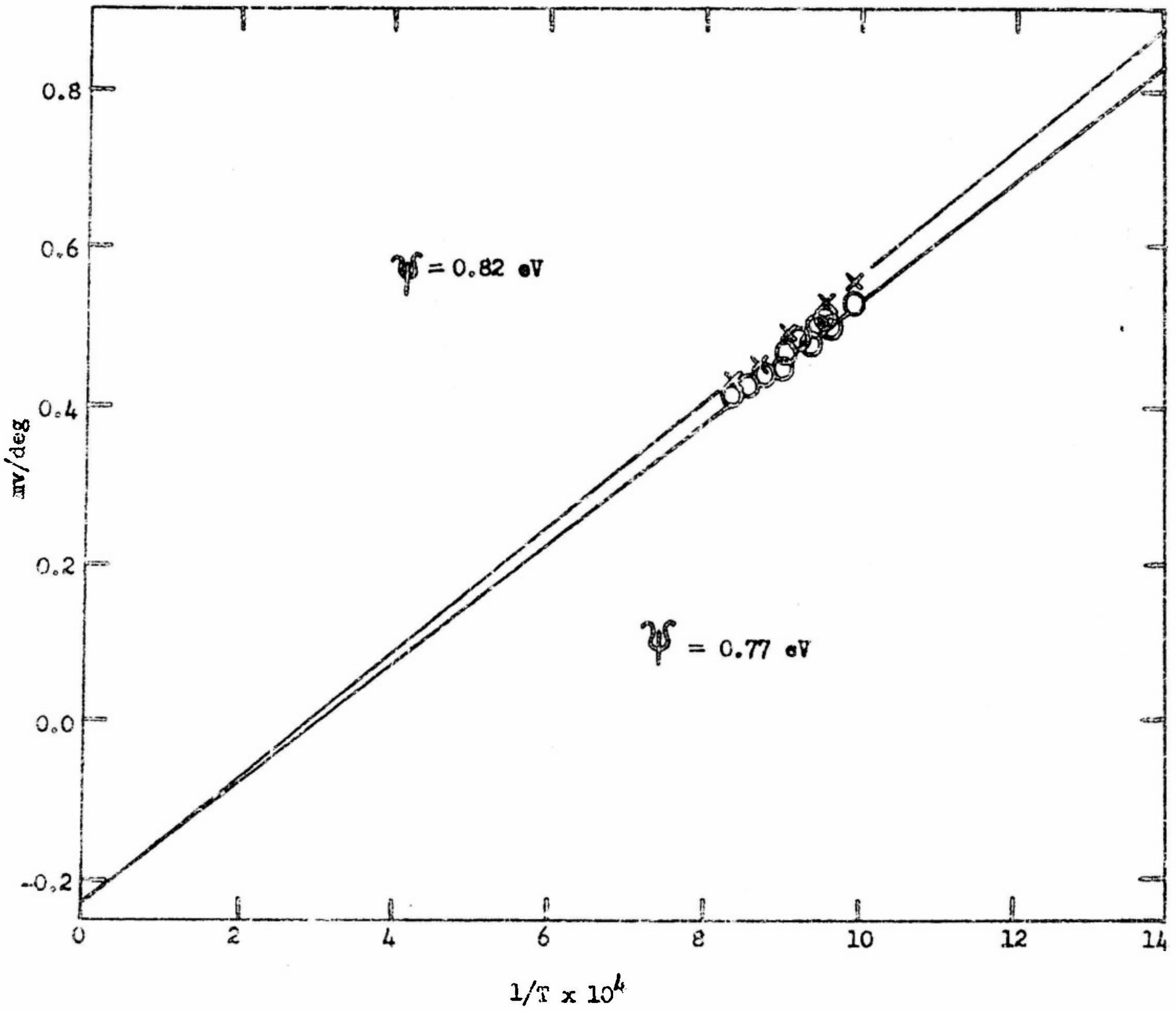
Only the measurements made in oxygen were sufficiently reproducible to be considered quantitative. The sign of the Seebeck effect in oxygen was such as to indicate p-type conduction. This would be expected on the hypothesis that absorption of oxygen creates thorium vacancies which serve as acceptor centers. Fig. 11 shows data from two different runs using the same crystal of thorium oxide. Thermoelectric power is plotted against reciprocal temperature. If the elementary theory were valid, one could compute from these curves, just as from conductivity curves, the energy gap and the density of impurity centers. As a matter of fact, one interesting fact was the agreement of gap values as deduced from the two kinds of measurement. Just as with conductivity, however, it seems definitely erroneous to assume for the oxygen case, that the density of impurity centers remains constant as the temperature varies. If this assumption is made, the computed density turns out to be unreasonably large, of the order of 10^{24}.

On the assumption that the simplest semi-conductor model is pertinent, equations for conductivity and thermoelectric power dV/dT are respectively (1) and (2).

$$\sigma = 2 e v n_0^{1/2} \left(\frac{2\pi m k}{h^2} \right)^{3/4} T^{3/4} \quad e^{\frac{E/2}{kT}} \tag{1}$$

$$\frac{dV}{dT} = \frac{k}{e} \left[2 + \frac{1}{2} \log \left(\frac{2\pi m k T}{n_0 \, h^3} \right)^{3/2} + \frac{E/2}{kT} \right. \tag{2}$$

Fig. 11 Thermoelectric Power of Thorium Oxide in an Atmosphere of Oxygen



If one could postulate that the density of impurity centers has a temperature dependence of the form

$$n_o = e^{\alpha - \frac{\beta}{kT}} \tag{3}$$

The above equations would become

$$\sigma = 2 e v e^{\alpha/2} \left(\frac{2 \pi m k}{h^2} \right)^{3/4} T^{3/4} \quad e^{-\frac{E/2 + \beta/2}{kT}} \tag{4}$$

$$\frac{dV}{dT} = \frac{k}{e} \left[2 - \frac{\alpha}{2} + \frac{1}{2} \log \left(\frac{2 \pi m k}{h^2} \right)^{3/2} T^{3/2} + e^{\frac{E/2 + \beta/2}{kT}} \right] \tag{5}$$

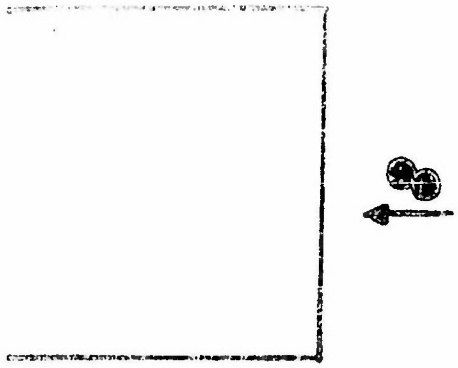
One sees that equality of slope is preserved; the equality of gap-values, calculated assuming (1) and (2) to be valid, would also obtain with (4) and (5) although the value so calculated would be incorrect.

Besides accounting for the equality of slopes, the assumption (3) can also give reasonable density of impurity centers.

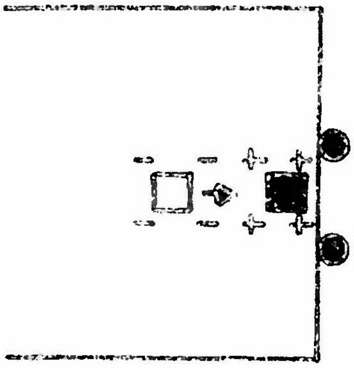
This assumption, however, requires that the density n_o be an increasing function of temperature as given in (3). If the impurity centers are thorium vacancies acting as donors, and produced as given in Fig. 15, such a function is conceivable.

A determination of the temperature dependence of n_o would be the next topic on this aspect of the program. It should obviously have precedence over any attempts to explain the results by more complicated semi-conductor mechanisms.

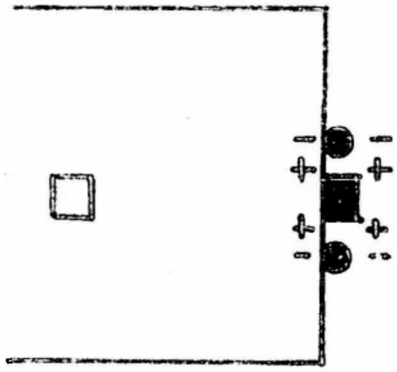
FIG. 15



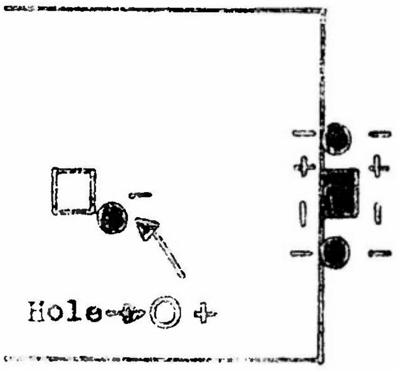
ThO$_2$ crystal with O$_2$ molecule approaching surface.



O$_2$ molecule adsorbed as atoms. Th^{++++} ion moves from nearby site to join them, leaving site negatively charged.



Adsorbed O atoms take 2 electrons each to become normal O ions in crystal. The vacancy is left neutral, migrates into crystal, may serve as acceptor for electron in valance band.



Electron leaves a normal state to occupy a state associated with the vacancy. A mobile electron vacancy (hole) is made available as a charge carrier.

5. Solubility of Hydrogen in Thorium Oxide Crystals

In a preceding section experiments were described involving the bleaching and conductivity change of a heated thoria crystal when the atmosphere around it was changed from oxygen to hydrogen. In order to understand further the role of hydrogen in causing the bleaching and lowered conductivity, it was felt necessary to determine whether the hydrogen could enter the thoria crystal in sufficient quantity to account for the changes observed. The red coloration is assumed to be due to the presence of excess oxygen which also produces p-type semi-conductor behavior. The most sensitive measurement available has failed to show any weight change associated with the reddening by oxygen of a crystal already in the white high-oxygen state, or the bleaching of a red crystal either in hydrogen or vacuum. The results of this work indicate an upper limit to the minimum oxygen change for bleaching in the neighborhood of 2×10^{17} atoms/cc of thoria. Measurement of the gas evolved when a crystal was bleached in vacuum indicated that this figure is of the correct order.

A number of oxygen-reddened crystals totaling 12 grams in weight were bleached at a temperature of 1000° C in hydrogen at one atmosphere pressure. They were then placed in a vacuum system with gas collection and analysis system attached. (This system is described in Reports of Contract NObsr-52592 dated November 15, 1951 and June 15, 1952). The crystals were heated to 1000° in this system, and the gas evolved measured and analysed. Successive runs of this experiment gave analyses of 80 percent, 120 percent and 95 percent as the hydrogen content of the evolved gas. The scatter, and the value above 100 percent are due to the inherent inaccuracy of the system when small quantities of gas are analysed. Thus we interpret the results as showing that substantially 100 percent of the gas evolved was hydrogen.

In the first run of this experiment, 2 mm^3 of gas (80 percent hydrogen analysis) were collected. In a subsequent run, made more carefully, it was seen that the quantity q evolved up to time t roughly followed the form $q = Q(1 - e^{-kT})$. The shape of the curve was not accurately fitted (perhaps due to variations of temperature of ± 30°). However, the asymptote seemed clearly enough indicated to enable one to determine the total quantity Q with reasonable accuracy. The total amount of gas dissolved in the thorium oxide crystals then turned out to be about 5 mm^3 (STP), which analysed about 100 percent hydrogen. The latter value was obtained twice. Taking the value of 5 mm^3 as most accurate, the amount of hydrogen dissolved in 1 cc of thorium oxide under the conditions initially given is about 2.5×10^{17} atoms. Thus it is found that the number of hydrogen atoms which enter the crystal when it is bleached are of the same order as the upper limit to the number of oxygen atoms required to be removed to effect bleaching. The close agreement is undoubtedly fortuitous, as none of the measurements involved pretend to this degree of accuracy.

6. Rectifying Properties of the ThO_2--Pt Contact

Further evidence regarding the nature of carriers, in addition to thermoelectric measurements and observations of effects of gaseous admixtures, was sought by observation of rectifying properties. In order to permit observations at elevated temperatures in an oxygen atmosphere, the metal contact was platinum.

Data were taken in oxygen and hydrogen. Rectifying properties were observed with the former, but not with the latter. Fig. 12 shows a plot of data taken in oxygen.

The sense of the rectification in the presence of oxygen indicated n-type conduction, a result which is inconsistent with the simple interpretation of the thermoelectric data and with the immediate interpretation of the fact of oxygen activation. Whether the inconsistency is due to incorrect choice of mechanism or due to incorrectly applied rectifier theory has not as yet been settled.

7. Dielectric Constant of Crystalline ThO_2.

No measurement of this quantity appears in the literature. Its value is of obvious interest in any general study of the material. For example, a very high temperature dependent value would suggest a molecular crystal structure with rotatable polar groups. Thin plates were cut from the crystals and measurements made at audio-frequencies. High accuracy was not easy to obtain with the small specimens. The value of the dielectric constant was found to be between 13 and 16. This is in line with other oxides ans suggests no unusual structure.

8. Hall Effect

Measurement of Hall effect in thorium oxide was not undertaken until near the end of the contract. It was felt that other phenomenological studies claimed prior importance. This proved to be the case, for example, as regards electrolysis and metallization of a crystal by passage of current. Hall data would be relatively meaningless unless the state and condition of the crystal were known at the time the measurements were made and much prior work was required in order that the state of a crystal be definable.

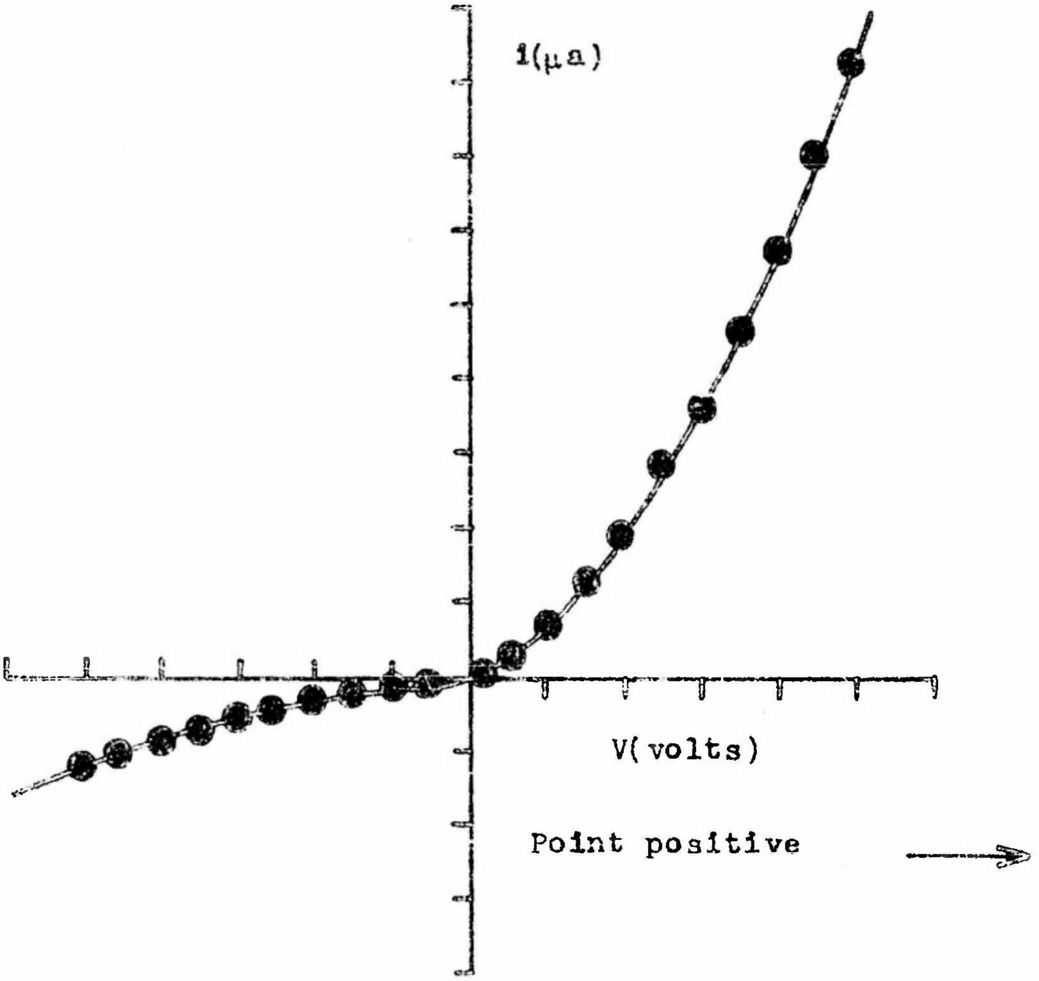


Fig. 12. Rectification at ThO_2-Pt contact at 750° C.

Work on Hall effect began about October 1, 1953 and the first matter considered was the method of heating. Naturally it would be desirable to carry the measurements up to temperatures used in thermionic applications, i.e. up to 1800° C. A direct approach might be to construct a high vacuum tube in which the specimen was mounted within a tungsten helix heated by 60 cycle A. C. The presence of the magnetic field of the order of 10^4 gauss would, however, introduce mechanical forces of serious magnitude. To use D. C. heating elements, as has been done in other high temperature Hall measurements, makes the problem a little simpler by removing vibration considerations. At the high temperatures we wished to use, however, the required currents become large and their supply and control is not convenient. Therefore, some time was spent experimenting with r. f. heating. Our 10 KW 450,000 cycle unit was available as a power source. A coupling transformer was improvised to get the desired impedance level in which the heater could be energized by r.f. current supplied through press leads in the same manner as 60 cycle power would be used. Continuous variation of the heating current could be achieved by constructing the transformer with variable coupling. Naturally, in using r.f. the possibility of pick-up was present. From the start, it was anticipated that special efforts might be required to eliminate this trouble.

In the first attempted Hall measurements, the specimen was a parallelepiped of crystalline thorium oxide, ground and polished, and mounted within a helical heating coil. Platinum coatings, evaporated on the ends, served as current electrodes. The Hall voltage was measured on platinum points held against the crystal by spring pressure. The use of platinum was necessitated by the desire to carry out the measurements in an oxygen atmosphere. As regards the magnet, the Foundation fortunately had in its equipment a watercooled electromagnet with 4" diameter polepieces and variable air gap. Fields of 15,000 gauss can be readily obtained.

Direct current was used in the specimen at first. Attempts to measure the probe voltage, (and, in particular, the changes of same when the field was reversed) were made with an L and N type K potentiometer and also directly with a galvanometer. Trouble was encountered with r.f. pick up, rectified at the probe contacts and appearing as a varying error in the probe reading. It became apparent that other measures must be taken. Some possible methods were (1) to shield the probes and leads from the r.f., (2) to tolerate the r.f. by using A.C. through the specimen and some means of detection, such as a tuned amplifier, which would be insensitive to the disturbance, (3) to abandon the r.f. heating and design apparatus which would withstand the mechanical forces encountered with D.C. heating.

Some cursory trials made it appear doubtful that method (1) was practical; complete shielding of the probe up to the point of contact was difficult.

Some work was done with method (2). A tuned amplifier was not available during the remaining time of the contract. However, an attempt was made, using 1000 cycle specimen current to measure the probe voltage with a difference amplifier as shown in Fig. 13. Trouble was encountered due to a circumstance which had not been anticipated, namely, that the r.f. supply had a pronounced 180 cycle modulation, which, with its harmonics, disturbed the output pattern of the difference amplifier. Therefore, a tuned

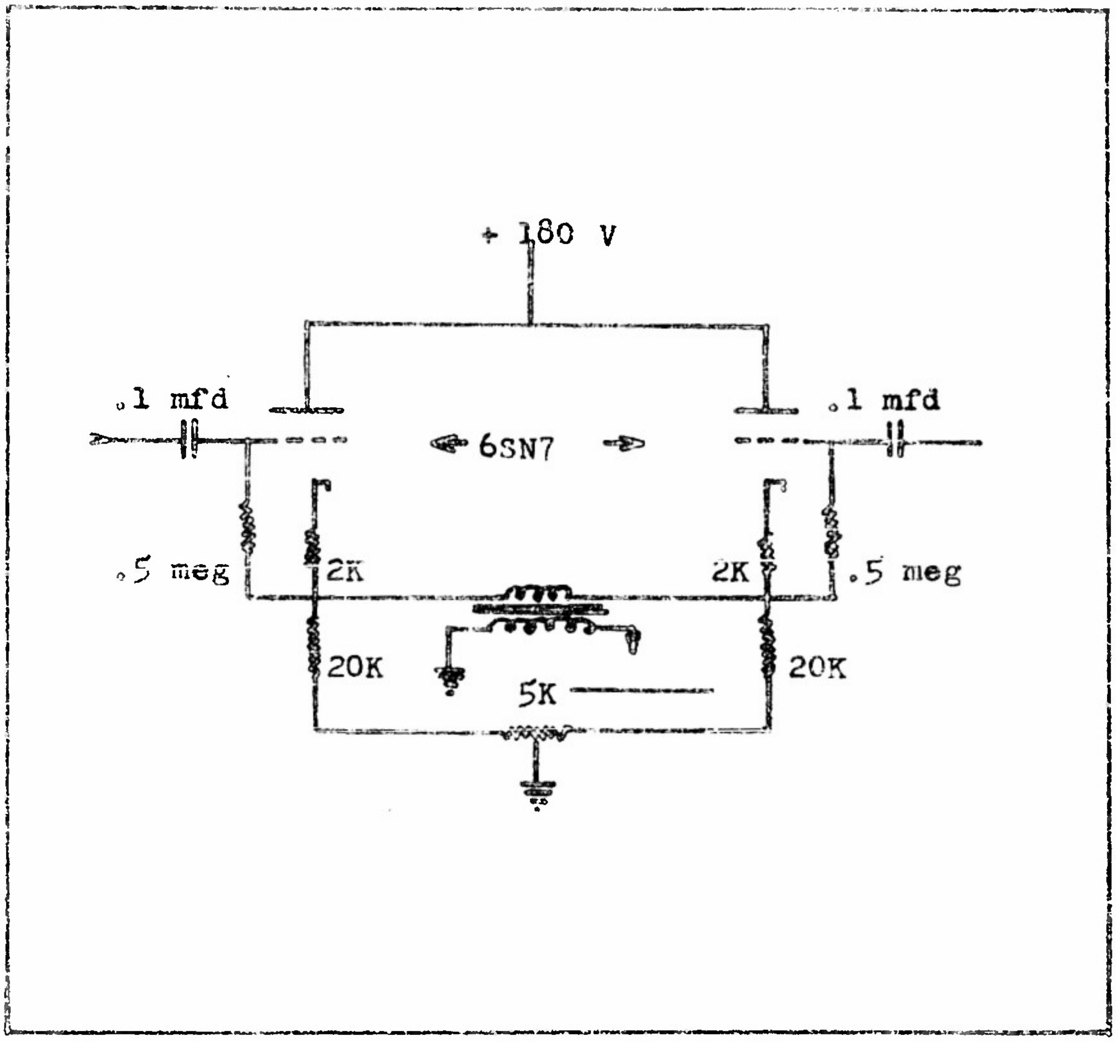


Fig. 13. Difference Amplifier, first stage.
Output General Radio type 4-1 transformer. Filaments heated with 6V storage battery.

amplifier seems essential if r.f. heating is to be employed. Equipment exists in the laboratory (a General Radio Wave Analyzer) which appears to be adaptable to this purpose and is undergoing some necessary reconditioning.

At the present time, however, it appears expedient to put aside the r.f. heating in the interest of obtaining, as soon as possible, data regarding the Hall effect in thorium oxide with excess oxygen. Therefore, we have, for the time being, turned to D.C. heating. The experimental arrangement now being used is shown in Fig. 14. In order to support the large mechanical forces which act upon the heating coil on account of the magnetic field, the coil is supported by a threaded ceramic form. Overall forces on this rigidly supported coil are eliminated by a bifilar type of winding.

As regards measurement of the D. C. probe voltages the use of a galvanometer directly is impractical because of the high resistance of the probe contacts. An electronic electrometer is being constructed for this purpose.

The above describes the status of our Hall studies at the termination of this contract. The work is being continued under the Office of Ordnance Research Contract DA-36-034-ORD-1487RD.

9. Studies with Silver Sulphide Crystals

Research which has as its ultimate objective the improvement of electron emission is primarily concerned with electronic phenomena rather than ionic. In thorium oxide, and to some extent in all semi-conductor emitters, the electronic phenomena are accompanied by ionic migrations. As regards applications, this shows itself

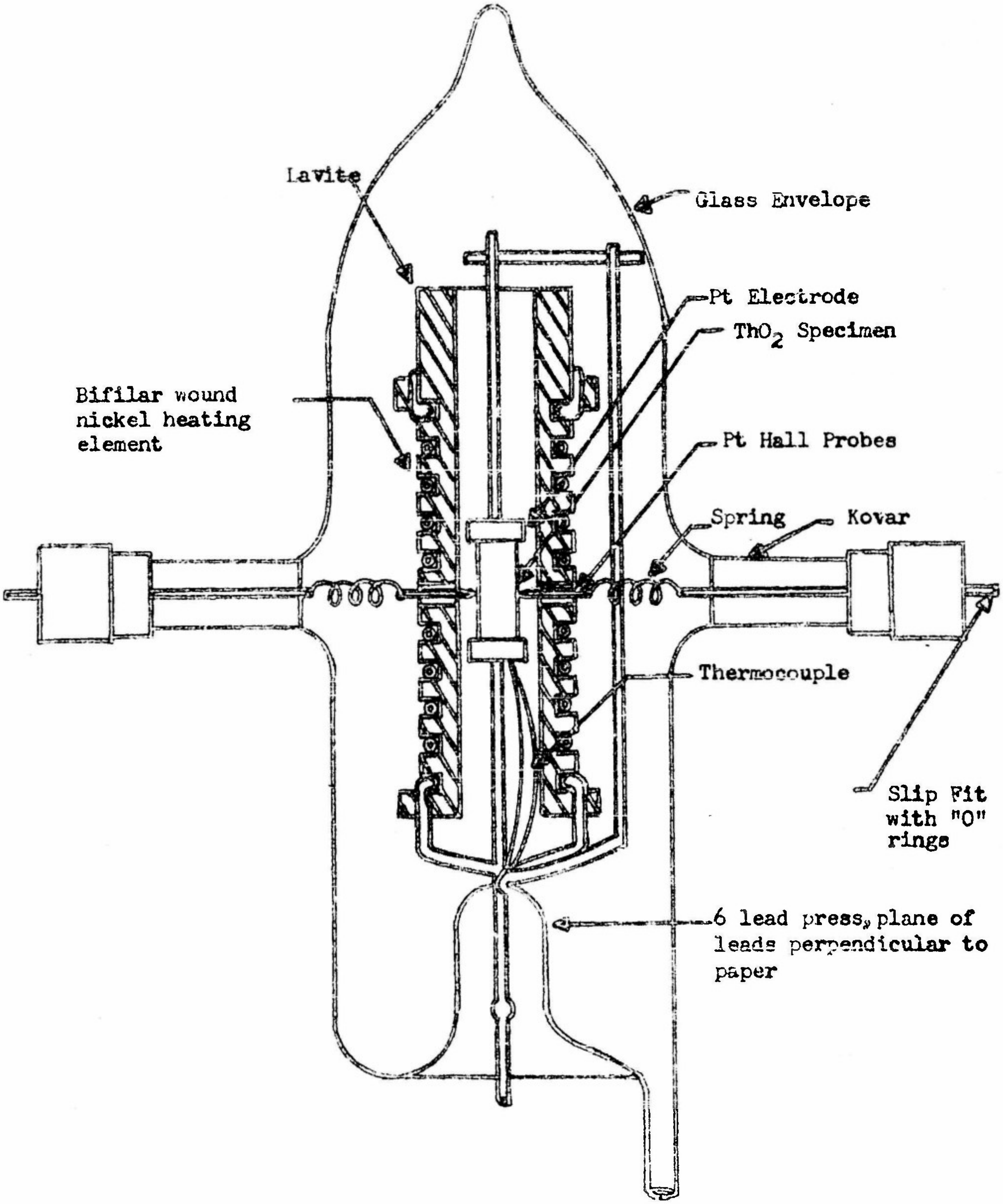


Fig. 14

Hall Effect Tube

primarily in the matter of electrolytic disintegration of cathode material. In the progress of research studies the ionic phenomena give rise, among other things, to time effects which may tend to obscure the electronic effect under investigation. Thus with thorium oxide, it becomes necessary to realize that we are dealing with mixed conduction, both electronic and ionic, and that when we are investigating phenomena of either kind we have to know how to interpret correctly the phenomena of the other kind.

Silver sulphide is a mixed conductor which has been considerably investigated by others; its mechanism of conduction is on the way towards becoming well understood. Therefore, by conducting experiments with silver sulphide which we are also conducting with the relatively poorly understood thorium oxide, we expect to have a valuable tool for the development and verification of the necessary theoretical concepts.

At the present writing, efforts are taking the form of attempts to grow single crystals of silver sulphide and some progress has been made although crystals of the desired size have not as yet been obtained. The material is being fused in quartz tubes and lowered slowly into the cooler region of the furnace.

The silver sulphide work has application both to the field of this contract (and its OOR successor) and to the Bureau of Ships Contract NObsr-52592. Personnel of both contracts are giving time to this aspect of the work.

10. Theoretical Summary

The preceding sections describe the experimental work which we have done with the object of understanding the energy level structure of thorium oxide. More experimental work pertinent to this objective remains to be done; quantitative theoretical formulations are still in a preliminary phase.

As the experimental work proceeded, attempts were made to interpret the results according to current theories. One makes the provisional hypothesis that the energy band picture of insulators and semi-conductors is relevant to thorium oxide. One further assumes tentatively that the conduction in oxygen, which appears to be p-type according to thermoelectric data, is due to thorium vacancies acting as acceptor centers. A process by which this might occur is shown in Fig. 15.

As regards the conduction in a non-oxygen atmosphere, the first hypothesis to suggest itself is, of course, that excess thorium produced by electrolysis provides donor centers.

Fig. 16 shows the customary model of a semi-conductor with filled band, conduction band, donors and acceptors. It should be emphasized that this model is recognized as oversimplified; it is being used primarily as a device for organizing the empirical data and as a starting point for development of an improved model.

We proceed, therefore, with a summary of our experimental results, the facts being classified according to the theoretical quantities to which they would pertain.

(a) Thermionic Work Function = ϕ

This quantity can be determined (except for uncertainties relative to the reflection coefficient) by determining field-free thermionic emission and solving the Richardson equation for ϕ.

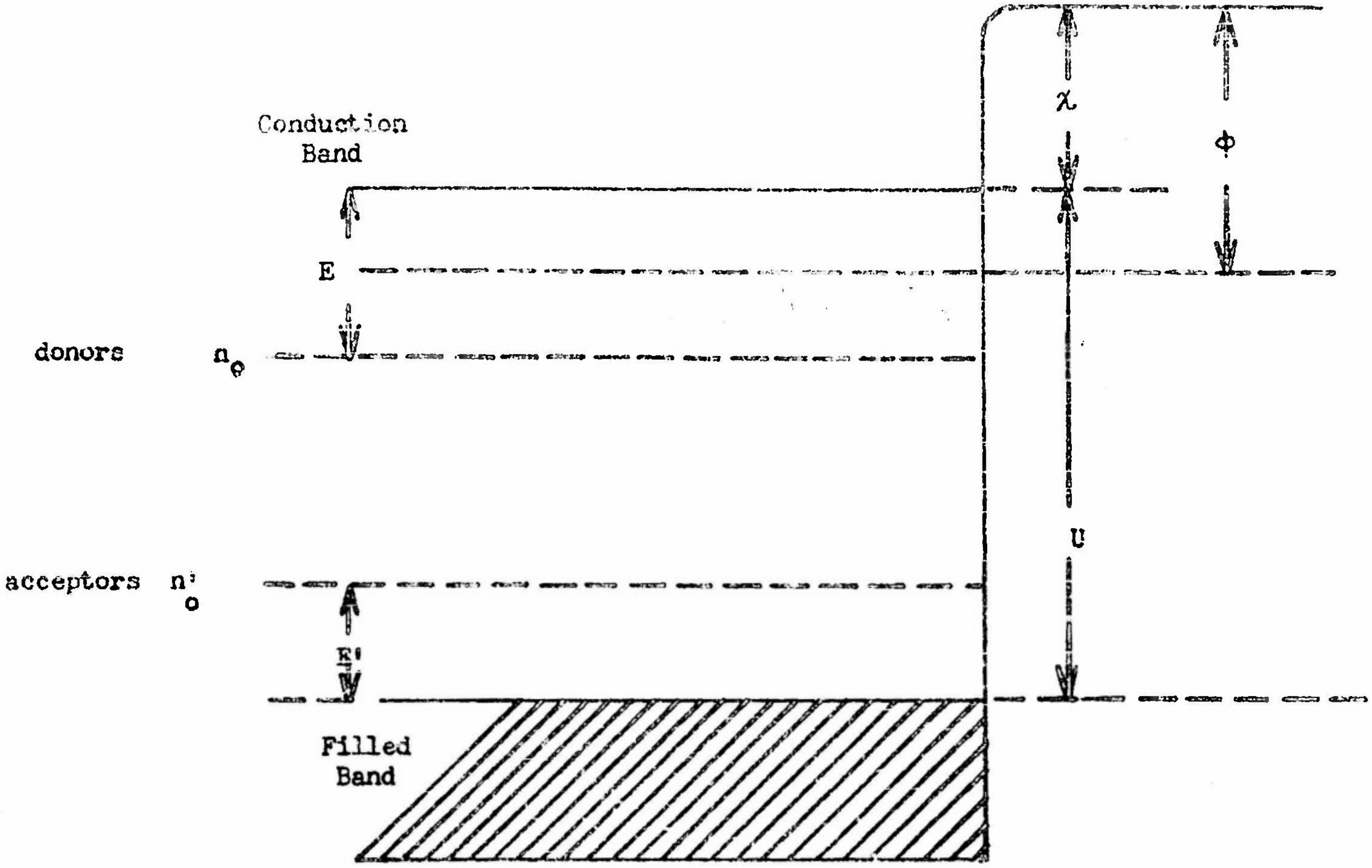


Fig. 16. The symbols on the diagram are defined as follows:

ϕ - Thermionic work function; Fermi energy referred to a zero outside the solid

χ - Electron affinity; potential of bottom of conduction band

n_o - Density of donor centers

n_o' - Density of acceptor centers

E and E' - Energies of donors and acceptors, as shown

U - Intrinsic energy gap

Estimates of the reflection coefficient must be arrived at by other means. Because of complications encountered with the tube for simultaneous measurement of conduction and thermionic emission, measurements of ϕ on single crystals have not been completed.

(b) Electron Affinity - χ

As with ϕ, the determination of χ involves thermionic measurements on single crystals and these studies have not as yet been carried out. The quantity χ, moreover, is not directly measured in the sense that ϕ may be. Its determination requires a theoretical model, and is, therefore, dependent upon the establishment of the model and determination of the several associated quantities.

(c) Intrinsic Energy Gap - U

Our approach to this quantity has been by means of ultraviolet absorption spectra. Assuming that the transmission cut-off corresponds to U (except for the correction necessitated by the Franck-Condon principle) we have measured a U value of 3.9 volts for the yellow, low-oxygen, form. The white and red, high-oxygen, forms of thorium oxide have a cut-off at about 3.3 volts. X-ray analysis has shown no difference of crystal structure between the two forms. It is, therefore, probable that 3.9 volts is the intrinsic gap in both cases and that the absorption between 3.3 and 3.9 volts for the high-oxygen material is due to the presence of excess oxygen. On this view, it is the low-oxygen crystal which has stoichiometric proportions.

(d) Energy intervals due to impurities (E and E')

Considerable progress has been made in the study of phenomena relevant to density of impurity centers (n_o and n_o') and to the associated energy intervals (E and E').

(1) Absorption maximum at 4000 Å, Low-oxygen form.

With the low-oxygen crystals, a high intensity absorption maximum is observed at 4000 Å. This would indicate an energy interval of 3.1 volts. The association of this absorption with impurity centers would thus require, for example, considerable density of donor centers close (i.e. 0.8 volts) to the filled band since this band disappears when oxygen is added. It is unlikely that foreign impurities are involved in this absorption band.

(2) Radiation reddening. Low-oxygen form.

A slight reddening of the yellow crystals can be produced by exposure to intense ultraviolet light of wavelengths below the cut-off ($\lambda < 3200$ Å). The absorbing centers so produced can be destroyed by exposure to radiation of wavelength greater than 4100 Å. Detailed spectral examination of this phenomenon is required both as regards its excitation and its destruction. Simultaneous conductivity measurements should be carried out.

(3) Conductivity and Thermoelectric Effects--Low-oxygen form.

Low-oxygen single crystals in vacuum show very pronounced time effects, presumably electrolytic. This has prevented the obtaining up to the present of numerical data regarding n_0 and E by conductivity and thermoelectric measurements.

(4) Radiation reddening, High-oxygen form.

A crystal which is reddened by baking in oxygen, will turn to clear white when heated in vacuum or hydrogen for a short time. The loss of oxygen in this process is unweighable and the crystal remains in what we call the high-oxygen form. Such a crystal will redden easily by exposure to radiation beyond the cut-off ($\lambda < 3700$). This coloration is destroyed by moderate heating, $T \sim 200^{\circ}$ C. It is thus strongly differentiated from oxygen reddening which is not destroyed by such heating.

(5) Conductivity, High-oxygen form.

In hydrogen, helium or vacuum, the slope of the $\log \sigma$ vs. $\frac{1}{T}$ curves indicates an activation energy of 1.3 volts. According to the simplest semi conductor assumptions this would give $E = 2 \times 1.3 = 2.6$ volts. Values of n_o of the order 10^{18} are obtained. In oxygen, assuming p-type conduction, and ignoring the possibility of n_o being temperature dependent, E' values of 1.5 volts are obtained, and values of n_o of the order of 10^{16}.

(6) Thermoelectric Effect - High-oxygen form.

In oxygen the phenomena were relatively stable and values of E' were obtained which agreed with those derived from conductivity measurements. In hydrogen and vacuum the phenomena were largely obscured by time effects, the magnitude of the effect was much smaller than in oxygen and it appeared to be of opposite sign, as would be expected.

(e) Density of Impurity Centers (n_o and n_o')

The types of phenomena which would lead to values of n_o

and n_o' include: (1) magnitude of the impurity-activated electrical effects, (2) direct measurement of amounts of added impurity, (3) quantitative interpretation of impurity activated optical absorption.

(1) Impurity activated electrical effects.

For thorium oxide in an oxygen atmosphere, temperature dependence of the conductivity yields $n_o' = 10^{16}$ per cm^3 based on simple theory. Under the same conditions and assumptions, thermoelectric data yield the absurd value of 10^{24} per cm^3. It is almost inevitable that, under conditions where the atmosphere is the activator, n_o' should be temperature dependent. Choice of a simple form for this dependence introduces another parameter and makes the picture formally consistent. The question as to whether the assumed form is theoretically justified is under consideration.

In a non-oxygen atmosphere (hydrogen, helium, or vacuum) the conductivity data yield values for n_o of the order of 10^{18}. Thermoelectric data under these conditions are not sufficiently consistent to give a determination.

The sign of the thermoelectric effects are such as to indicate p-type conduction in oxygen and probably n-type in the other cases.

The sense of rectification at a platinum contact, however, is inconsistent with the above; it indicates n-type conduction in oxygen. The interpretation of the rectification effects is, however, somewhat more uncertain than for the thermoelectric effects.

When the hydrogen atmosphere is replaced by the oxygen atmosphere, the conductivity at 1000° K increases by a factor of 4 in a time of several seconds. Quantitative consideration of this in terms of probable values of diffusion coefficients remains to be done. Pressure dependence of the conductivity in an atmosphere of oxygen has been determined. A mass action calculation predicts a 1/5th power dependence. The observed power law was 1/6 in one case, and 1/7.9 in another.

(2) Direct Measurement of Activating Substance

In the absence of oxygen, activation is provided by impurities originally present and by products of electrolysis.

In an oxygen atmosphere, it has been found (by subsequent loss of weight in vacuum at high temperatures) that a crystal will absorb of the order of 10^{18} oxygen atoms per cc. The number involved, however, in the change from red to white color, and in the associated reduction of conductivity is small compared to this and is established as $< 2 \times 10^{17}$ per cm^3. That is, the weight of an oxygen-red crystal is not measurably different from that of one which has been vacuum (or hydrogen) bleached just to the point where the oxygen-activated conductivity has disappeared.

(3) Quantitative Interpretation of Optical Absorption

This aspect of our work is as yet undeveloped. Quantitative spectrometer observations of impurity-activated absorption, combined with their mathematical interpretation, remains to be done. The types of phenomena concerning which this effort might be worth while are: radiation reddening of high-oxygen crystals, reddening of high-oxygen crystals by current drawing.

IV. FUTURE INVESTIGATIONS

1. Measure conductivity of radiation-reddened low-oxygen crystal during bleaching by 4000 A radiation.
2. Work function of flat surface of crystal of known crystal orientation. Conduction can be determined non-simultaneously.
3. Seek ThO_2 crystal of higher purity, e.g. set up oxalate process for purifying 100 lbs. of material, have fused by Norton Company. Investigate crystalization from molten solutions as a purifying means.
4. Measure absorption coefficient in the 3.9 - 3.1 volt region with oxygen rich crystals as functions of pressure and temperature.
5. Do precise pulsed measurements of conductivity of low-oxygen crystals in vacuum as a function of temperature to obtain gap values for comparison with optical results.
6. Vary oxygen pressure with oxygen-rich crystal and observe conductivity and color simultaneously. Determine whether the increase of conductivity when oxygen is added is related to the change from white to red.
7. Verify whether bleaching of a red crystal in vacuum and bleaching by hydrogen are both simply accounted for by loss of oxygen.
8. Observe reddening by passage of current, and using data from (6), calculate rate of production of electrolytic oxygen.
9. Measure conductivity vs. time when oxygen atmosphere is applied, and relate data to diffusion coefficients.

10. In connection with (9) measure diffusion coefficient of thorium metal in a thorium oxide crystal.

11. Complete Hall measurements in oxygen; extend to higher temperatures in vacuum.

12. Investigate further the validity of the assumption $n_o = e^{\alpha - \beta/kT}$ as density of acceptor centers in oxygen atmosphere.

V. PUBLICATIONS

1. "Optical Properties of Crystalline Thoria", O. A. Weinreich and W. E. Danforth, Phys. Rev. Vol. 88, No. 4, 953-954, Nov. 15, 1952.

2. "Thorium Oxide and Electronics", W. E. Danforth, Advances in Electronics Vol. V, 1953 (Academic Press, Inc., New York, N. Y.).

A paper entitled "Electrical Conduction and Thermoelectric Power in Thorium Oxide Crystals," by O. A. Weinreich and W. E. Danforth was presented at the Durham, North Carolina meeting of The American Physical Society, March, 1953.

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Optical Properties of Crystalline Thoria

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(Received July 30, 1952; Revised copy received October 1, 1952)

THE optical properties of fused transparent crystalline thoria have been investigated. Spectroscopic analysis of the crystals showed that their purity is comparable to that of mantle grade thorium nitrate and standard thorium metal. The purity is estimated to be in the vicinity of 99.9 percent. Rather complex changes of the absorption spectrum could be observed when the specimen was heated in vacuum, oxygen, or hydrogen. Figure 1 shows the absorption spectrum (uncorrected for reflection) of a thoria crystal, which has been taken through the following cycle: (a) heating to 1800°C in vacuum, (b) heating to 1000°C in air, (c) heating to 1000°C in vacuum, (d) reheating in vacuum at 1800°C.

Heating in oxygen or air reddens the crystal and following heating in vacuum or hydrogen at 1000°C results in bleaching. The ultraviolet cutoff for these states is at 3700A. This fundamental absorption may be associated with the gap between the filled band and conduction band. The change of the absorption curve following the heating to 1000°C in vacuum (curves *a* or *d* in Fig. 1) is characterized by: (1) a shift in the ultraviolet cutoff from about 3700A to 3200A, and (2) the appearance of a sharp absorption peak at about 4000A.

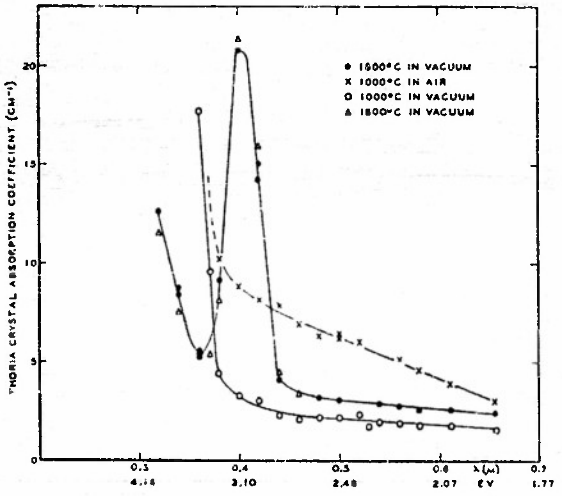

FIG. 1. Optical absorption of crystalline thoria.

Tentatively, we relate this absorption peak to the presence of excess thorium (oxygen deficiency) of the specimen. Consistent with this hypothesis are weight changes, which are found when alternating the 1000°C oxygen and 1800°C vacuum treatment. The weight changes account for intake or release of approximately 10^{18} oxygen atoms per cc. The weight changes have been checked by gas analysis. No measurable weight changes, however, could be found, when the 1000°C oxygen and 1000°C vacuum treatment were alternated. We refer to these crystals as oxygen-rich. Oxygen-rich crystals bleached in vacuum or hydrogen turn red when exposed to light in the region just beyond the cutoff. The trapping centers for the radiation-produced reddening are shallow; bleaching occurs at 200°C in vacuum.

Another variety of color is obtained by rapid quenching which results in a deep black color. These crystals are opaque in the measured spectral range from 0.2 to 2μ.

No photoconductivity has been observed for any of the described crystals at light intensities, where that of diamond is easily detected.

Measurements pertinent to the mechanism of electrical conductivity of oxygen-poor thoria specimens have been recently published.[1] In this case part of the current is electrolytic, causing rapid decomposition of the crystal. Measurements of electrical conductivity with oxygen-rich crystals were made at 1100°C in oxygen of atmospheric pressure. In contrast to the oxygen-poor specimen, no electrolytic decomposition is detected.

It is a pleasure to acknowledge the services of Harry Bleecher, who developed the necessary polishing techniques and prepared the specimens

---

[1] W. E. Danforth, Phys. Rev. **86**, 416 (1952).

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