

of the polarization curves herein presented. These results were prepared, however, not only to exhibit the effects to be expected in this case but were intended also to be illustrative of the general behavior of the polarization in the neighborhood of such a resonance.

The author does believe, however, that the situation in regard to helium scattering is still fluid in spite of the careful work of Bashkin *et al.* on the total cross section and will so remain until crucial experiments on the differential cross section have been performed.

## Electrical Resistance of Thoria

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Measurements of the electrical conductivity of thoria were taken in vacuum at temperatures up to 2073°K. Activation by passage of current resulted in values of resistance as low as 1 ohm-cm at 1900°K and 10 ohm-cm at 1000°K. Activation energies between 3.2 volts and 0.58 volt were found. The density of impurity centers was computed as  $10^{18}$  per cc and was found to be independent of the degree of activation by current, a result which is inconsistent with the hypothesis of the electrolytic origin of impurity centers.

### I. INTRODUCTION

**S**TUDIES of the electrical conductivity of thoria have obvious practical interest as regards cathode design and performance. In addition, there are several objectives of a theoretical nature. An understanding of the conduction mechanism is a necessary step in the understanding of the mechanism of thermionic emission and also of the causes of the disintegration of cathode material by passage of current. Previous investigations have been made by Foex<sup>1</sup> whose values of resistance are much higher than those we have found and by Wright<sup>2</sup> who briefly reported some data which have been found to fit satisfactorily into the general pattern of our observations.

### II. EXPERIMENTAL PROCEDURE

Our measurements have been taken on sintered sleeves of thoria, mounted between molybdenum end pieces as indicated in Fig. 1. The material was molded to size and sintered. It was not pressed. The density was approximately 7 g/cm<sup>3</sup>. Currents up to 7.6 amp./cm<sup>2</sup> were passed through the specimens and potentials were measured at the probe leads, by oscilloscope for pulsed data, and high resistance voltmeter for the dc runs. Pyrometer readings were made on the inside of the specimen through a hole in one of the end pieces.

The specimens were mounted in a small vacuum furnace whose main features are shown in Fig. 2. The thoria piece, whose length was about 2 cm and outside diameter 3 mm, was supported within a coil of 60 mil tungsten.

The data to be presented were taken with this furnace mounted in a water-cooled copper jacket which was continuously pumped on a mercury system. Since

the system contained one soft-soldered joint, it could not be baked at high temperature but was maintained at 100°C for 24 hours. Pressures were below  $10^{-7}$  mm with a cold specimen but would rise to  $5 \times 10^{-6}$  mm at a specimen temperature of 1800°C, the maximum used at present.

### III. RESULTS

Figure 3 shows the results of measurements taken on a specimen prepared from C.P. thoria from Eimer and Amend. Before any current was passed through the thoria it was outgassed at 1800° for several hours. Then runs of resistance *vs.* temperature were taken using single pulses, produced by a simple condenser discharge arrangement, and an oscilloscope.

For each one of these curves, several runs were taken, a smooth curve was drawn through the data, and points from this average curve were transferred to the logarithmic plot. The probable error estimated from the spread of the data is about 10 percent.

As shown in Fig. 3a, it was found that the data from pulse measurements require two exponential components, one with activation energy of 0.86 volt and the other of 3.2 volts. Activation energy is here defined as the quantity  $E$  in the Eq.  $\sigma = \sigma_0 e^{-E/kT}$ .

One must remember, of course, that we have a porous, sintered, specimen and not a crystal. It is perhaps appropriate, therefore, (following Loosjes and Vink<sup>3</sup>) to ascribe the low activation energy, the one predominant at the low temperature, to conductance through the solid particles, and the high temperature portions of the curve with a work function of 3.2 to thermionic emission across the interstices.

The pore-conduction hypothesis, however, is by no means established in the present case. It would, in fact,

<sup>1</sup> M. Foex, *Comptes Rendus* **215**, 534 (1942).

<sup>2</sup> D. A. Wright, *Proc. Phys. Soc. London* **B62**, 188 (1949).

<sup>3</sup> R. Loosjes and H. J. Vink, *J. App. Phys.* **20**, 884 (1949).

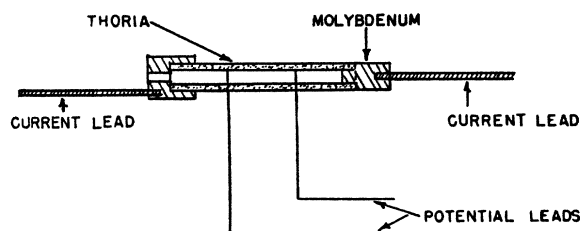


FIG. 1. Arrangement of conductivity specimen.

be just as plausible to assign the 3.2 volt activation to an intrinsic excitation. Spectroscopic evidence for the required intrinsic level is being sought.

Passage of 0.076 amp./cm<sup>2</sup> dc through the specimen causes immediate increase of conductivity by a large factor, after which the situation appears to be dominated by a single activation energy of 1.0 volt.

It is interesting to notice that the data of Wright<sup>2</sup> happen to fall within the probable error on this curve which we find as an activation state corresponding to a current density of 0.076 amp./cm<sup>2</sup>.

Increasing the dc density further to values of 0.76 amp./cm<sup>2</sup> and then to 7.6 amp./cm<sup>2</sup> produced successive increases of the conductivity until values of resistivity as low as 1 ohm-cm at 1900°K and 10 ohm-cm at 1000°K were obtained. A specimen thus activated may be directly heated from room temperature by passage of current.

One naturally cannot take too seriously the application of semi-conductor theory to these sintered specimens. However, it may be of interest to note the following: As Wright has pointed out, if one uses the relation  $n = \sigma / ev$  where  $\sigma$  is the conductivity,  $n$  the number of conduction electrons,  $e$  their charge, and  $v$  their mobility, and if one assumes a mobility of 10 cm/sec. per volt/cm one finds  $10^{16}$  conduction electrons per cc at 1900°K. Then using the Fowler equation<sup>4</sup> with the observed activation energies one computes a density of impurity centers of  $10^{18}$  per cc.

If we apply this same calculation to our most highly activated state we have the interesting result that the increase in conductivity produced by this increase of current is not accompanied by an increase in the number of impurity centers but would follow entirely from the observed decrease of activation energy. Otherwise stated, different conditions of activation by current show different values of  $E$  but the coefficient  $\sigma_0$  tends to remain constant.

<sup>4</sup>  $n = n_0 \frac{1}{2} \left\{ \frac{2\pi mkT}{h^2} \right\}^{\frac{1}{2}} \exp(-U/2kT)$ , where  $n$  = density of impurity centers. The quantity  $U/2$ , one half of the energy band separation, is equal to the observed slope of the curve of  $\log \sigma$  vs.  $1/T$  and is thereby empirically determined. There is admittedly some question as to whether the above equation is appropriate for analysis of this data or whether one should use the other limiting case in which the number of impurity centers is in excess of the number of available electrons (see N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, 1940), Chapter V, Section 2). Pending further evidence in this matter, the simpler expression was chosen.

This result, that the activation by a current does not increase the number of impurity centers, is of course contrary to the view that the activation is caused by electrolysis of the material. Also it is questionable whether the electrolysis theory can explain the fact that the increase of activation takes place very quickly, in a few seconds. The time required to produce  $10^{18}$  atoms even with our highest current of 7.6 amp./cm<sup>2</sup> will be several minutes if the percent ionic conduction is as low as we believe it to be; that is,  $10^{-4}$  ion per electron. With our lowest current (0.076 amp./cm<sup>2</sup>) the calculated time exceeds the observed time by a factor of more than one thousand.

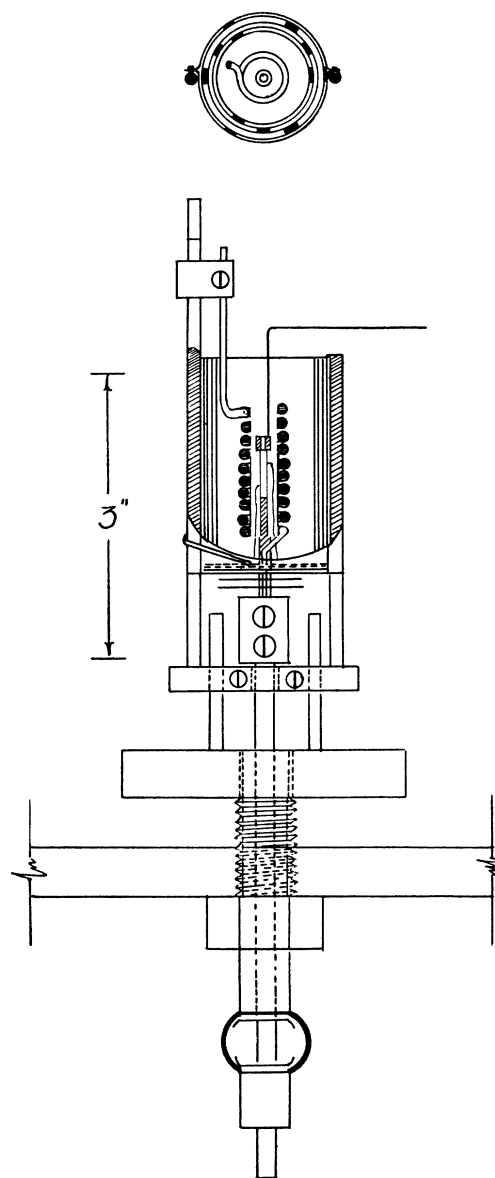


FIG. 2. Vacuum Furnace. The specimen is mounted within a tungsten coil which is surrounded by five coaxial molybdenum heat shields.

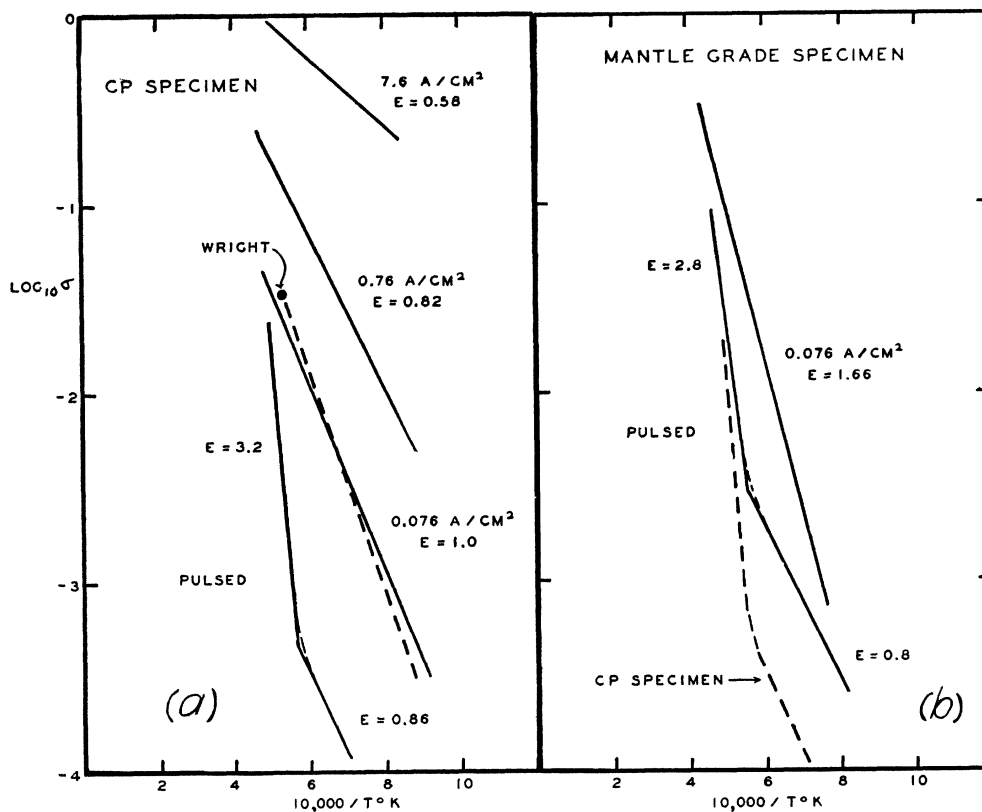


FIG. 3. Conductivity ( $\sigma$ ) in  $(\text{ohm-cm})^{-1}$  for different states of activation-by-current. The curves marked *pulsed* represent data before any dc was permitted to flow. Values of  $E$  are activation energies in electron-volts.

On Fig. 3b we have data taken with mantle grade thoria, the dashed lines representing C.P. data from the preceding figure. As one might expect, the initial conductivity before activation by current is less for the purer material. At higher temperatures, where perhaps

some intrinsic phenomenon are occurring, the two materials give more nearly equal values of conductivity.

It is a pleasure to acknowledge the skilled services of Harry Blecher, who constructed the apparatus and assisted in taking the measurements.