

and 1:9 mixtures from  $\text{pH}$  3.5 to 4.8 is a 3% increase in height, indicating that there is very little change in either the 1:1 or 1:9 system in this  $\text{pH}$  range.

In Fig. 3C it is seen that from  $\text{pH}$  3.5 to 4.5 the absorbance at 434  $\text{m}\mu$  of the 1:1 uranyl-tartrate mixture increases 10%, whereas that of the 1:9 uranyl-tartrate mixture increases only 2%. The explanation for the larger slope in the 1:1 curve appears to be that there is present in the 1:1 mixture above  $\text{pH}$  3.5 a small amount of a species with a combining ratio greater than unity. The absorbance of the 1:9 solution at 434  $\text{m}\mu$  is exceeded by the 2:1 and 3:1 absorbances at about  $\text{pH}$  3.6, respec-

tively, and the  $\text{pH}$  effect on the 2:1 and 3:1 spectra is very large.

The existence of all three uranyl-tartrate complexes near  $\text{pH}$  4.6 is evident from the 1:1, 2:1 and 3:1 spectra in Fig. 1D. The spectrum of each of these solutions has the same contour as at  $\text{pH}$  3.5 (compare Fig. 1D with 1C), the wave lengths of peaks and shoulders being unchanged.

The spectrophotometric results which have been obtained above  $\text{pH}$  5 will be reported in a subsequent paper along with potentiometric titration data, because of the very close link between the interpretation of these two studies.

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## Absorption Spectra and Electrical Conductivities of $\text{UO}_2$ - $\text{ThO}_2$ Solid Solutions<sup>1</sup>

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The absorption spectra of  $\text{UO}_2$ - $\text{ThO}_2$  solid solutions between 4500 and 7000  $\text{\AA}$ . show four discrete bands with maxima at 5100, 5400, 6000 and 6500  $\text{\AA}$ . which are attributed to electronic transitions between various states of the  $\text{U}^{4+}$  ion. In addition, an intense, continuous absorption band is found whose long wave length edge shifts to shorter wave lengths with decreasing uranium concentration. This band is attributed to resonance of uranium ions between different oxidation states. Electrical conductivities of pressed  $\text{UO}_2$ - $\text{ThO}_2$  discs were measured for the temperature interval 300-450°K. and were found to decrease by a factor of  $10^6$  in the concentration range 100-10% uranium. The activation energy for conductivity changed from 0.20 e.v. for pure  $\text{UO}_2$  to 0.37 e.v. for 10%  $\text{UO}_2$ -90%  $\text{ThO}_2$  solid solution. An attempt has been made to correlate changes in the optical and electrical properties with nearest neighbor interactions involving uranium ions in different oxidation states.

Although progress in the field of oxidic semiconductors has been rapid,<sup>2</sup> there is as yet no comprehensive theory concerning the mechanism of electronic conduction in these materials. As an aid to the development of such a theory, the "dilution" technique may play an important role since it allows one to introduce the concentration of the semiconducting species as a parameter which can be varied over a wide range at will. The procedure consists of forming solid solutions between a semiconductor ( $\text{UO}_2$ ) and an insulator ( $\text{ThO}_2$ ) and studying relevant properties as a function of the concentration of the semiconducting ingredient. In the present investigation, the absorption spectra and electrical conductivities of a series of  $\text{UO}_2$ - $\text{ThO}_2$  solid solutions ranging from pure  $\text{UO}_2$  to 2.5%  $\text{UO}_2$  were measured. These compounds are isomorphous and form a continuous range of solid solutions with the fluorite structure.<sup>3</sup>

### Experimental

**Preparation of Solid Solutions.**—Two methods were used for the preparation of solid solutions, both leading to the same results. The first method was essentially identical with that of Trzebiatowski and Selwood.<sup>3</sup> The dried hydroxides were pressed into discs (0.5" diameter and 1" long) in a stainless steel mold at a pressure of 10 tons/in.<sup>2</sup> and then fired at 1500° for 8 hours in a hydrogen atmosphere. The second method consisted of intimately mixing  $\text{UO}_2$  and  $\text{ThO}_2$  in a ball mill, pressing the mixture into discs and firing at 1750° in hydrogen for 8 hours. This procedure was repeated to ensure the formation of solid solution. In all

cases, the samples were cooled to room temperature in hydrogen. The X-ray parameters determined on both sets of samples were in good agreement with the previous measurements<sup>3</sup> and showed that true solid solutions were formed. Since the samples fired at 1750° possessed greater mechanical rigidity, they were used in all of the measurements. Spectroscopic analysis of the starting materials showed them to be free (<0.01%) of transition and rare earth metal impurities.

**Measurements of Absorption Spectra.**—Two techniques were employed for measuring the absorption spectra of the oxides. The first was to incorporate approximately 10 mg. of the oxide into 200 mg. of KBr by grinding in an agate mortar and then pressing the mixture into a 0.5" diameter disc. A modification of this technique has been described in detail in the literature<sup>4,5</sup> where it has been applied to infrared spectra of organic materials. It promises to be a useful tool for the investigation of the spectra of inorganic solids as well. The second technique was to affix a disc of the fired oxide to a thin 0.5" diameter quartz plate by means of Canada balsam and, using optical grinding methods, to reduce the thickness of the oxide disc to the point of light transmission. The final thickness of the oxide film turned out to be 0.001" for pure  $\text{UO}_2$  and  $\approx 0.005$ " for 10%  $\text{UO}_2$ -90%  $\text{ThO}_2$ . A Cary spectrophotometer was used for obtaining the spectra. Both methods of obtaining the spectra gave identical results. Discs of  $\text{ThO}_2$  were used as blanks.

Spectra were obtained at liquid nitrogen temperatures by mounting the samples in a dewar of a design similar to one described in the literature.<sup>6</sup>

**Measurement of Electrical Conductivities.**—Resistances were measured with a Leeds and Northrup Type S Test Set. The samples were 0.5"  $\times$  0.25" discs cut from the original oxide bodies with a carborundum wheel. They were ground flat on an optical block. The samples were held between platinum plates by means of two 0.5" diameter aluminum rods of equal length. Surrounding the sample and the aluminum rods was a nichrome wound furnace 5"

(1) Presented in part at the Fall, 1953, Meeting of the American Chemical Society, Chicago, Ill.

(2) J. L. Snoek, "New Developments in Ferromagnetic Materials," Elsevier Pub. Co., New York, N. Y., 1947.

(3) W. Trzebiatowski and P. W. Selwood, *THIS JOURNAL*, **72**, 4504 (1950).

(4) M. M. Stimson, *ibid.*, **74**, 1805 (1952).

(5) U. Schiedt, *Z. Naturforsch.*, **76**, 270 (1952).

(6) R. Caster, P. Fringsheim and P. Yuster, *J. Chem. Phys.*, **18**, 887 (1950).

in length at whose center the sample was situated. The temperature of the furnace could be controlled to within  $\pm 1^\circ$  and was constant to  $\pm 2^\circ$  for 1" in either direction of the midpoint. A chromel-alumel thermocouple placed within  $\frac{1}{8}$ " of the sample was used in conjunction with a Rubicon potentiometer as a temperature measuring device. The whole assembly, furnace aluminum rods, platinum discs and sample was placed between the platens of a Carver Laboratory press and a pressure of 500 lb./in.<sup>2</sup> was applied.

### Results and Discussion

The prevailing view of oxidic semiconductors is that they owe their conduction properties to the presence in the crystalline lattice of defects of one sort or another. In those oxides in which there is a stoichiometric excess of oxygen over metal it has been shown in some cases,  $\text{UO}_2$  for example,<sup>7</sup> that the Hall coefficient is anomalous. DeBoer and Verwey<sup>8</sup> postulated a conduction mechanism for oxides of this type which assumed the preservation of a perfect anion lattice and the creation of a certain number of positive ion vacancies. Preservation of electroneutrality demands that an equivalent number of cations be oxidized to a higher oxidation state, these being "bound" in energetically the most favorable state, to cation vacancies. Conduction is then thought of as the "thermal" freeing of positive holes with the setting up of chains of the type  $\text{M}^+-\text{M}^{++}-\text{M}^+$ . The ease of formation of positive ion vacancies must be closely associated with the energy of the ionization process  $\text{M}^+ \rightarrow \text{M}^{++} + e$  and so it is not surprising to find semiconducting

properties chiefly among the oxides of the transition metals where such processes are energetically most favorable.

It is a well-known observation that the semiconducting transition metal oxides are intensely colored. Despite the widespread occurrence of this phenomenon, no detailed theoretical basis has yet been advanced for it. The color is commonly said to be due to electronic resonance among the various oxidation states of the cations in the crystal. The connection between the optical and electrical properties is strikingly illustrated in the case of NiO. Pure stoichiometric NiO is light green and has a conductivity of  $10^{-8} \Omega^{-1} \text{ cm.}^{-1}$ . Upon the addition of a few hundredths of a mole per cent. of excess oxygen, however, the color turns black and the conductivity is increased by a factor of  $10^4$ .<sup>8</sup>

#### Absorption Spectra of $\text{UO}_2$ - $\text{ThO}_2$ Solid Solutions.

—The room temperature absorption spectra of pure  $\text{UO}_2$  and of the  $\text{UO}_2$ - $\text{ThO}_2$  solid solutions in the region 4500–7000 Å. are reproduced in Fig. 1. Along the ordinate is plotted the optical density in arbitrary units. The most striking results of dilution are the shift of the long wave length edge of the continuous absorption band to shorter wave lengths and the simultaneous appearance of structure previously hidden by the continuous absorption. Recently, Kröger, *et al.*,<sup>9</sup> made very similar observations in a study of the reflection spectra of NiO-MgO solid solutions. The maxima of light absorption in the 10%  $\text{UO}_2$  solution are approximately at 5100, 5400, 6000 and 6500 Å. The band at 6500 Å. is present in all the samples studied. It is shifted to shorter wave lengths with increasing dilution. (Visually, the colors of the oxides range from brown for pure  $\text{UO}_2$  through green to olive-green for 10%  $\text{UO}_2$ .) No splitting or sharpening of the bands was observed in the spectra taken at liquid nitrogen temperatures. The band structure of the samples dilute in uranium is reminiscent of that found in other quadrivalent uranium salts.<sup>10</sup> It may be tentatively concluded that these absorptions are due to processes in which the electronic configuration of the  $\text{U}^{+4}$  is changed without the liberation of electrons. The continuous intense absorption, on the other hand, apparently represents an electron process of a different sort. The following discussion deals with a point of view regarding this latter process which may prove to be of some interest. In  $\text{UO}_2$ , each cation and therefore each cation vacancy is surrounded by 12 nearest neighbor uranium ions (fluorite structure). Of the 12 nearest neighbors surrounding a vacancy, 8 will be in the +4 oxidation state while 4 will be in the +5 oxidation state so as to preserve electroneutrality. (The argument would remain the same in principle if it were assumed that 10 of the ions were in the +4 state and 2 in the +6 state.) Electronic interchange takes place easily between the 12 cations adjacent to the lattice hole so that in reality no distinction can be made between +4

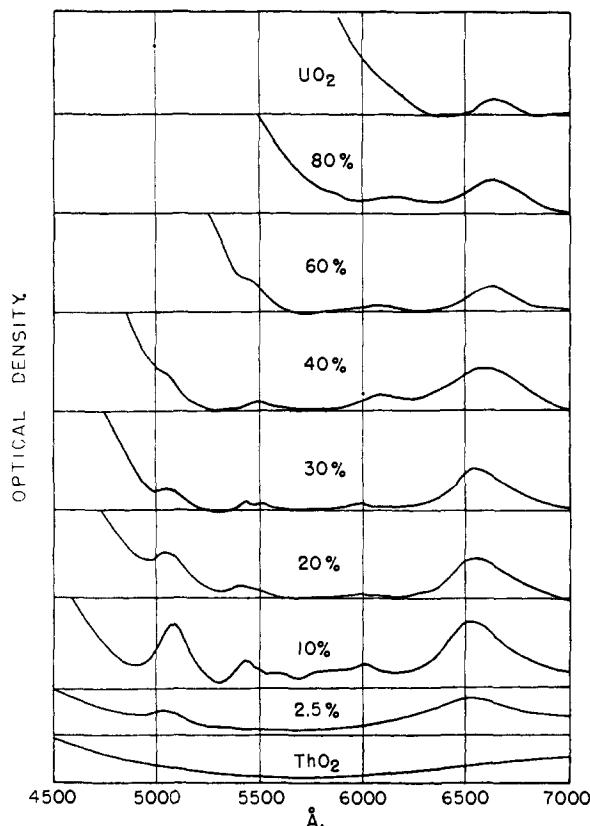


Fig. 1.—Absorption spectra of  $\text{UO}_2$ - $\text{ThO}_2$  solid solutions.

(7) W. Hartmann, *Z. Physik*, **102**, 709 (1936).

(8) J. H. DeBoer and E. J. W. Verwey, *Phys. Soc. London*, **49**, 59 (1939).

(9) F. A. Kröger, H. J. Vink and J. Van Den Boomgaard, *Physica*, **18**, 77 (1952).

(10) F. Ephraïm and M. Mezener, *Helv. Chim. Acta*, **16**, 1257 (1933).

and +5 uranium ions. The device of speaking of different oxidation states in this case is simply a convenient way of indicating the absence of a certain number of electrons. The primary resonance structure, which neglects all except nearest neighbor interactions, is composed of 12 uranium ions sharing 20 electrons in unfilled shells, since each  $\text{U}^{+4}$  ion has 2 unpaired electrons and each  $\text{U}^{+5}$  ion has 1 unpaired electron. Such a structure we assume possesses a system of continuous electronic energy levels in contradistinction to the band structure associated with isolated, non-resonating  $\text{U}^{+4}$  or  $\text{U}^{+5}$  ions. Let us examine the consequences of relating the continuous intense absorption in  $\text{UO}_2$  and in the  $\text{UO}_2\text{-ThO}_2$  solid solutions with the resonance of uranium ions between two oxidation states. Substitution of diamagnetic  $\text{Th}^{+4}$  for  $\text{U}^{+4}$  in the lattice has the effect of decreasing the stability of the resonance structures because  $\text{Th}^{+4}$ , having a fixed oxidation state, cannot enter into electron exchange. Figure 2 is a plot of the shift of the long wave length edge of the continuous absorption as a function of the uranium concentration. The shift amounts approximately

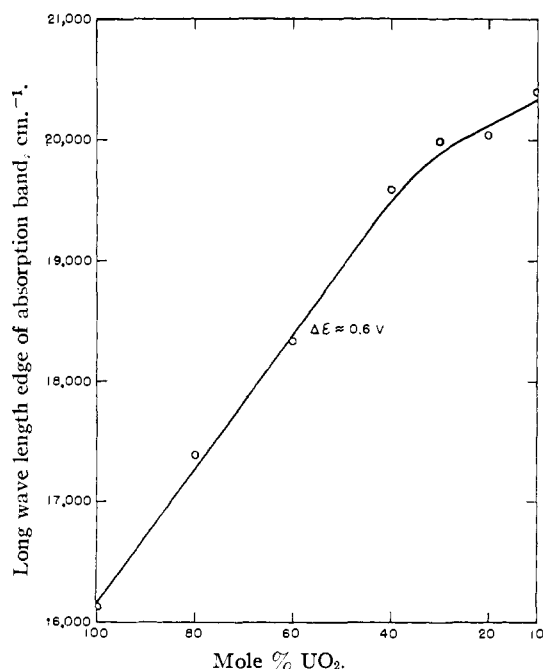


Fig. 2.—Shift of the long wave length edge of the continuous absorption band as a function of the uranium concentration.

to 0.6 electron volt in going from pure  $\text{UO}_2$  to 10%  $\text{UO}_2$ . The shift is rapid in the region 100–40% uranium, but levels off in the region 40–10% uranium. One can calculate statistically,<sup>11</sup> assuming random replacement of uranium by thorium, the fraction of  $\text{U}^{+4}$  ions having  $n$  or more up to 12  $\text{U}^{+4}$  ion nearest neighbors, etc. Figure 3 is a graph of such a calculation. From this graph it can be seen that at 60 mole per cent.  $\text{UO}_2$ , 0.95 of the  $\text{U}^{+4}$  ions are surrounded by 5 or more  $\text{U}^{+4}$  ions; this fraction has dropped to 0.55 at 40 mole per cent. and to 0.02 at 20 mole per cent.  $\text{UO}_2$ . In order for

(11) P. Niggli, *Helv. Chim. Acta*, **30**, 1452 (1947).

nearest neighbor resonance of the sort  $\text{U}^{+4} \rightleftharpoons \text{U}^{+5} + e$  to occur, at least 5 nearest neighbor uranium ions must surround each vacancy. The primary resonance structures, therefore, are largely eliminated in the region 100–40%  $\text{UO}_2$ . Since the effect on the continuous absorption is most pronounced in this region, the primary resonance structures must be responsible for the major portion of the absorption. Effects at still lower concentrations are then due to decreased interactions among next nearest neighbors.

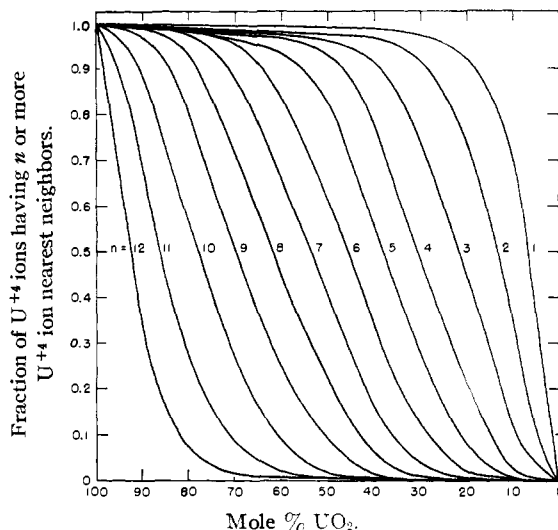


Fig. 3.—Fraction of  $\text{U}^{+4}$  ions having  $n$  or more  $\text{U}^{+4}$  ion nearest neighbors as a function of the uranium concentration.

**Electrical Conductivity of  $\text{UO}_2\text{-ThO}_2$  Solid Solutions.**—The negative logarithms of the specific electrical conductivities are plotted in Fig. 4 as a function of  $1/T$ . The observed resistances were

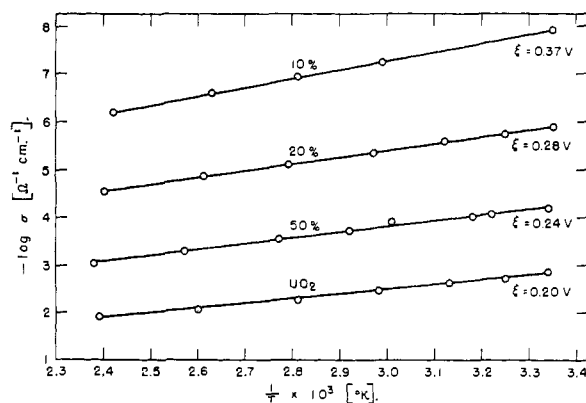


Fig. 4.— $-\log \sigma [\Omega^{-1} \text{cm.}^{-1}]$  vs.  $1/T \times 10^3 [^\circ\text{K.}]$  for various  $\text{UO}_2\text{-ThO}_2$  solid solutions.

converted after dimensional measurements of the pressed discs to specific conductivities,  $\sigma$ , by means of the equation

$$\sigma = h/Rg$$

where  $h$  is the height of the disc in cm.,  $g$  is its area in  $\text{cm.}^2$  and  $R$  is the measured resistance in ohms. Activation energies,  $\epsilon$ , in electron volts were calcu-

lated for each experiment according to the equation

$$\epsilon = 1.99 \times 10^{-4} \frac{\log \sigma_1 - \log \sigma_2}{1/T_2 - 1/T_1}$$

The conductivity isotherm at 300°K. and the activation energy is plotted as a function of the uranium concentration in Fig. 5. In the range 100–40%  $\text{UO}_2$ , the conductivity decreases only by a factor of 10 and the activation energy increases 0.05 e.v.

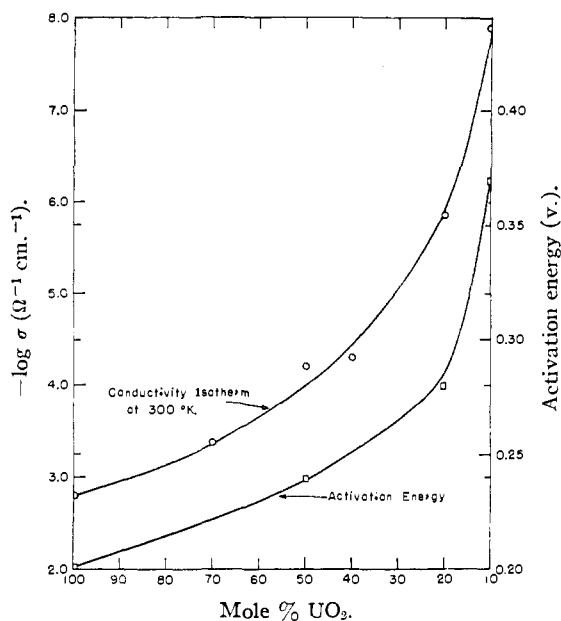


Fig. 5.—Conductivity isotherm at 300°K. and activation energy as a function of the uranium concentration.

Between 40–10%  $\text{UO}_2$ , however, the conductivity decreases by a factor of  $10^4$  while the activation energy increases 0.12 e.v. Calculations show that it is possible to account for the observed conductivities to within  $\pm 10\%$  assuming a fixed value of  $A$  ( $\approx 4\Omega^{-1} \text{cm.}^{-1}$ ) in the relation  $\sigma = Ace^{-\epsilon/kT}$  over the whole concentration range,  $c$ , of uranium. This indicates that the number, mean free path and mobility of the carriers is not greatly altered by the replacement of thorium for uranium and that the decrease in conductivity is almost solely due to the increase in activation energy. It already has been

stated that the major effect of dilution on the electrical properties occurs in the region 40–10%  $\text{UO}_2$ . This may be understood in terms of a picture based on the DeBoer-Verwey electronic conduction mechanism.<sup>8</sup> The primary resonance structure in  $\text{UO}_2$  of 12 uranium ions surrounding a cation vacancy is stabilized by the resonance energy of the process  $\text{U}^{+4} \rightleftharpoons \text{U}^{+5} + e^-$ . Processes of this type recently have been discussed<sup>12</sup> and have been called “double exchange.” The exchange energies have been estimated to be of the order of several tenths of electron volts.<sup>13</sup> Conduction in  $\text{UO}_2$  occurs by the thermal activation of an electron from a normal  $\text{U}^{+4}$  lattice site to the primary resonance structure and the consequent setting up of chains  $\text{U}^{+5}-\text{U}^{+4}-\text{U}^{+5}$ , etc. The cation vacancy thus acts as an “impurity level.” As thorium is introduced, the resonance stabilization energy is decreased, thus increasing the energy gap between the full band and the “impurity level.” At around 40%  $\text{UO}_2$ , nearest neighbor resonance becomes impossible (Fig. 3 and previous discussion) and one might expect a rather sudden decrease in the stability of cation vacancies. This point has been discussed by the author<sup>14</sup> in another connection. In a study of the electrical conductivity of  $\text{U}_3\text{O}_8-\text{ThO}_2$  solid solutions, Hund and Niessen<sup>15</sup> observed a discontinuity in the activation energy at around 24% uranium which they interpret on the basis of a change from an ideal cation to an ideal anion lattice. In the case of the  $\text{UO}_2-\text{ThO}_2$  solid solutions, however, it is likely that the ideal anion lattice prevails and that the same conduction mechanism operates over the whole concentration range. It would be desirable to study other systems which meet the same simplifying conditions.

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