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THE SULPHIDES, SELENIDES, AND TELLURIDES OF TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM

III. ELECTRICAL PROPERTIES

By F. K. McTaggart

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Summary

The resistivities, types of conduction, thermo-e.m.f.'s, and rectifying ability of the sulphides, selenides, and tellurides of the elements Ti, Zr, Hf, and Th were determined. A wide range of properties was found and the variations reflect the trend within this group of compounds from semimetallic in the case of Ti to metallic in the case of Th. The transition from non-metallic to metallic affinities that occurs from sulphur to tellurium is likewise evident.

I. Introduction

Previous investigators of these systems concerned themselves almost entirely with the consideration of phases and phase regions, and to a lesser extent with crystal structure and changes in molecular volumes. There was even much disagreement about the phases present. Some reactions of the materials with acids, alkalis, and oxidizing agents had been noted but nothing appeared to be known concerning the electrical properties of this substantial group of compounds beyond statements by Strotzer, Biltz, and Meisel (1939) and Eastman *et al.* (1950) to the effect that ZrS_3 and ThS_2 seemed to be non-conductors of electricity, and a claim by the latter authors that ThS, Th_2S_3, and Th_7S_{12} had specific resistivities of 10^{-3} to 10^{-4} Ωcm. Many of the investigations had been made with impure materials, especially those involving the thorium chalcogenides, and few of the workers noted that all these materials are subject to at least surface oxidation in the air at room temperatures.

It was decided to investigate the resistivity, type of conduction (metallic, N or P semiconduction), thermoelectric power, and rectifying properties of each of the phases between $AX_{1\cdot0}$ and $AX_{\text{max.}}$ now known to exist in the 12 systems comprising the sulphides, selenides, and tellurides of titanium, zirconium, hafnium, and thorium, using the preparations described either by McTaggart and Wadsley (1958), or investigated more recently (McTaggart, unpublished data).

II. Materials

Most of the compounds, namely, the chalcogenides of titanium, zirconium, and hafnium, have already been described in some detail (McTaggart and Wadsley 1958). They are listed in Table 1, which shows the broadly descriptive type

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* Division of Industrial Chemistry, C.S.I.R.O., Melbourne.

name (e.g. diselenide etc.), appearance, formula, etc. The thorium compounds are also presented in the same manner. The materials were all finely divided powders, about one-third of which were smooth to the touch and graphitic in nature. In addition to these were single crystals, obtained by sublimation: TiS_3 in the form of ribbons of approximate maximum dimensions 1 cm by 0·25 mm by 0·01 mm; $ZrTe_3$ in the form of needles 0·5 cm by 0·5 mm; $TiTe_2$ in the form of plates 2 by 2 mm.

III. MEASUREMENTS AND RESULTS

(a) *Specific Resistivity*

The resistivities of the powders were determined by compressing them between steel plungers in dies of clear plastic material and measuring resistances with either a Thomson bridge (for resistances below 2 Ω) or by direct determination of voltage and current (for resistances above 2 Ω). A pressure equivalent to 25,000 lb/in^2 was chosen; at this pressure the distortion of the plastic die was negligible and the value of resistance measured was no longer subject to rapid change with pressure. The agreement between specific resistivity values so obtained and those found by measurements on single crystals was reasonably good. With TiS_3, for example, where the regular shape of the ribbon-like sublimed crystals permitted their dimensions to be determined very accurately with the aid of a micrometer microscope, the specific resistivity (Sp.K.) of single crystals measuring approximately 0·5 cm by 0·2 mm by 0·008 mm was 2·0 to 2·4 Ωcm, whereas the average value for compressed TiS_3 powder was 6·0 Ωcm. The other single crystals gave even closer agreement with the corresponding compressed powders. Duplicate measurements on a single sample invariably yielded values differing by not more than 10 per cent. and agreement between values obtained from powders representing different syntheses of the same compound was surprisingly good, for example, $TiSe_2$, 0·0020 and 0·0018 Ωcm: $ThTe_{1\cdot 0}$, 0·02 and 0·023 Ωcm; $ZrSe_3$, 18,000 and 23,000 Ωcm. Hence, it is considered that the values have a degree of reliability such that conclusions may be drawn from them concerning the nature of the compounds.

The Sp.K. values for the various preparations (Table 1) are shown graphically in Figure 1. The lines joining the points do not necessarily represent intermediate values but are drawn to show the trend in Sp.K. and to enable the eye to follow each metal-chalcogen system.

The main difficulty encountered was the rapid oxidation of several of the preparations. It had been noted in earlier attempts to make measurements on compacts of the materials that the resistance of them increased with time. Some of the compounds, such as $TiTe_{1\cdot 0}$ and $ZrTe_{1\cdot 0}$, were pyrophoric. In such cases the measurements were carried out in an argon atmosphere.

As an example of the effects of oxidation on the measured Sp.K. value, ZrS_2 may be cited. A fresh preparation of this material, opened and tested in argon, had a Sp.K. of 10 Ωcm. When a portion was left in the air, its Sp.K. rose rapidly as shown in Figure 2, and eventually became relatively steady at about 20,000 Ωcm. Another portion of the material was placed in oxygen at 9·5 °C and the amount of oxygen absorbed was measured. This gave the

TABLE 1

PROPERTIES OF THE CHALCOGENIDES

Material	Formula	Appearance	Specific Resistivity (Ωcm)	Thermo-e.m.f. (mV/°C)	Type of Conduction
Titanium					
Trisulphide ..	$TiS_{2\cdot95}$	Dark blue - black ribbon crystals*	6·0	0·6	N semi
Disulphide ..	$TiS_{1\cdot95}$	Dark bronze*	0·008	0·2	N semi
Sesquisulphide	$TiS_{1\cdot50}$	Black	0·001	—	Metallic
Monosulphide..	$TiS_{1\cdot00}$	Dark grey-brown	0·001	—	Metallic
Subsulphide† ..	$TiS_{0\cdot50}$	Black	0·0003	—	Metallic
Diselenide ..	$TiSe_{2\cdot00}$	Dark purply brown*	0·002	—	Metallic
Sesquiselenide	$TiSe_{1\cdot50}$	Black	0·0005	—	Metallic
Monoselenide	$TiSe_{1\cdot00}$	Black	0·0005	—	Metallic
Subselenide† ..	$TiSe_{0\cdot50}$	Black	0·0002	—	Metallic
Ditelluride ..	$TiTe_{2\cdot00}$	Black*	0·0001	—	Metallic
Sesquitelluride	$TiTe_{1\cdot50}$	Black*	0·0005	—	Metallic
Monotelluride..	$TiTe_{1\cdot00}$	Black*	0·0005	—	Metallic
Subtelluride† ..	$TiTe_{0\cdot50}$	Black, brown tinge	0·0002	—	Metallic
Zirconium					
Trisulphide ..	$ZrS_{2\cdot95}$	Orange*	200,000	1·0	N semi
Disulphide ..	$ZrS_{2\cdot00}$	Brown-violet*	10	0·7	N semi
Sesquisulphide	$ZrS_{1\cdot50}$	Black	0·08	0·05	N semi
Monosulphide..	$ZrS_{1\cdot0}$	Dark grey-black	0·006	—	Metallic
Triselenide ..	$ZrSe_{3\cdot05}$	Black, purple tinge*	20,000	1·0	N semi
Diselenide ..	$ZrSe_{1\cdot95}$	Dark greyish green*	0·10	0·3	N semi
Sesquiselenide	$ZrSe_{1\cdot50}$	Black	0·007	0·05	N semi
Monoselenide	$ZrSe_{1\cdot00}$	Very dark grey	0·004	—	Metallic
Tritelluride ..	$ZrTe_{2\cdot90}$	Black lustrous*	0·0004	—	Metallic
Ditelluride ..	$ZrTe_{1\cdot70}$	Dark purple-brown bronze	0·001	—	Metallic
Sesquitelluride	$ZrTe_{1\cdot50}$	Black	0·0016	—	Metallic
Monotelluride..	$ZrTe_{1\cdot00}$	Black	0·001	—	Metallic
Hafnium					
Trisulphide ..	$HfS_{3\cdot00}$	Bright orange*	100,000M	—	(?) semi
Disulphide ..	$HfS_{2\cdot00}$	Purple-brown	1000M	—	(?) semi
Sesquisulphide	$HfS_{1\cdot50}$	Light yellow-brown	150	0·2	N semi
Monosulphide..	$HfS_{1\cdot00}$	Black	0·50	—	Metallic
Triselenide ..	$HfSe_{2\cdot90}$	Black*	80,000	—0·4	P semi
Diselenide ..	$HfSe_{1\cdot85}$	Very dark brown	20	0·25	N semi
Sesquiselenide	$HfSe_{1\cdot50}$	Black	6	0·2	N semi
Monoselenide	$HfSe_{1\cdot00}$	Black	0·15	—	Metallic
Sesquitelluride	$HfTe_{1\cdot50}$	Black	0·015	—	Metallic
Monotelluride..	$HfTe_{1\cdot00}$	Black	0·004	—	Metallic

* Indicates graphitic materials.

† Not necessarily distinct phases.

TABLE 1 (*Continued*)

Material	Formula	Appearance	Specific Resistivity (Ωcm)	Thermo-e.m.f. (mV/°C)	Type of Conduction
Thorium					
Polysulphide	$ThS_{2\cdot50}$	Light red-brown	5000M	—	(?) semi
Disulphide ..	$ThS_{2\cdot00}$	Brown	10,000M	—	(?) semi
$MX_{1\cdot7}$ type ..	$ThS_{1\cdot70}$	Green-grey	25,000	0·2	N semi
Sesquisulphide	$ThS_{1\cdot50}$	Dark grey	10	0·1	N semi
Monosulphide..	$ThS_{1\cdot00}$	Dark grey	0·2	—	Metallic
Polyselenide ..	$ThSe_{2\cdot50}$	Dark purple	10,000	—0·8	P semi
Diselenide ..	$ThSe_{2\cdot00}$	Dark grey	150,000	—0·5	P semi
$MX_{1\cdot7}$ type ..	$ThSe_{1\cdot70}$	Black	400	0·25	N semi
Sesquiselenide	$ThSe_{1\cdot50}$	Black	4·0	0·1	N semi
Monoselenide	$ThSe_{1\cdot00}$	Black	0·06	—	Metallic
Polytelluride	$ThTe_2$	Black*	4·0	—	N semi
Ditelluride ..	$ThTe_{2\cdot00}$	Black	0·02	—	Metallic
Sesquitelluride	$ThTe_{1\cdot50}$	Black	0·015	—	Metallic
Monotelluride..	$ThTe_{1\cdot00}$	Black	0·02	—	Metallic

* Indicates graphitic materials.

results shown in the second curve in Figure 2. It will be seen that 1·75 c.c. O_2/g ZrS_2 (approx. 0·25 per cent. by weight) was absorbed in 7 days, causing a 2000-fold increase in resistivity. There is another interesting feature of this compound. That the oxygen adsorbed formed a surface layer was shown by the behaviour of either of the above samples during compression. Each pressure increment caused a large momentary decrease in resistance as shown in Figure 3 where current is plotted against pressure in the first section. The current peaks were probably considerably higher than those shown, as a moderately damped meter was used. The lower points represent the value of the current 30 sec after the pressure increment was applied. Finally, at a constant pressure of 120,000 lb/in², the current decreased with time as shown on the second section of the graph. Apparently each pressure increase resulted in the shearing of the particles of ZrS_2, the oxide layer thereby being disturbed, resulting in lowered resistance. The subsequent increase in resistance and the shape of the curve on the right-hand side of Figure 3 suggest a rapid reoxidation of the ZrS_2. If the sulphide, after surface oxidation had taken place, was pumped to a high vacuum and subsequently opened and the compression test carried out in an argon atmosphere, the current increased on compression as before but showed considerably less decrease with time. If when being pumped the material was heated to about 300 °C prior to opening the testing in argon, the peaks were not observed at all, and the sulphide was found to have a Sp.K. value corresponding to the highest values obtained after the surface oxidation had taken place. Zirconium sesquisulphide and some hafnium compositions behaved similarly, but none of the titanium sulphides did.

(*b*) *Type of Conductivity*

Measurements were made to determine whether, in the range 20 to 80 °C, the compounds exhibited metallic or semiconduction. At the conclusion of each Sp.K. test, the plungers compressing the material were heated to 80 °C and the resulting change, if any, in resistance was noted. Four or five heating cycles were carried out. For the reason discussed above, some of the samples had to be measured in argon. The method did not yield very precise results and it was possible to distinguish only between compounds whose conductivity increased noticeably (5 per cent. or greater) and those whose conductivity remained substantially the same or showed a slight decrease. The results are

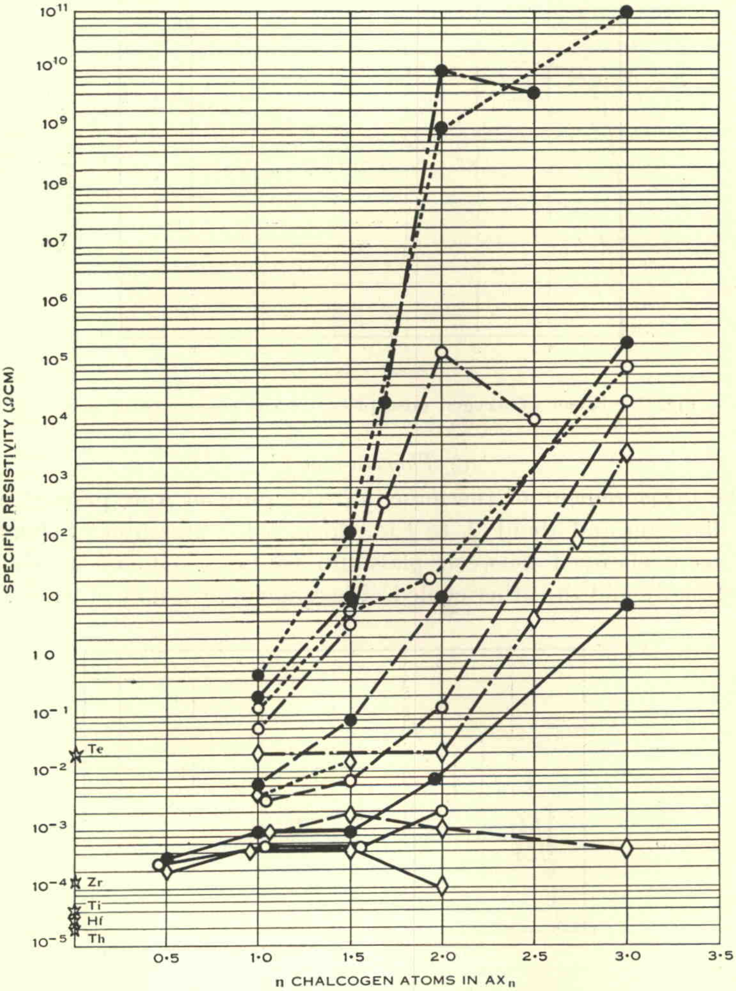

Fig. 1.—Specific resistivities of the chalcogenide compounds. —— Titanium; – – zirconium; - - - hafnium; ·—· thorium; ● sulphide; ○ selenide; ◊ telluride; ✡ specific resistivities of the pure metals.

included in Table 1. Where semiconduction was evident the type, N or P, is noted, this having been determined as described below. Most of the tri- and disulphides and triselenides exhibited conductivity increases of 2 to 4 times in the temperature range used.

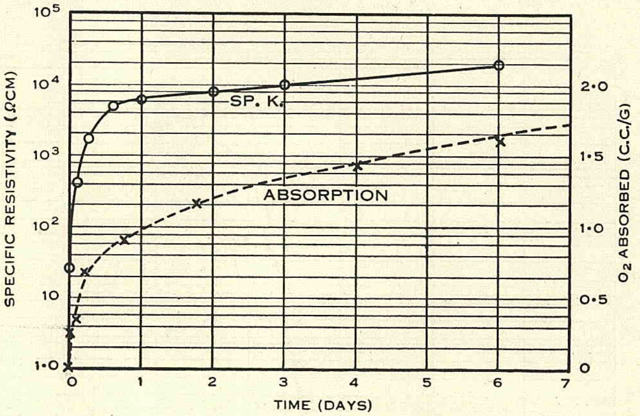

Fig. 2.—Effect of oxygen adsorption on the resistivity of ZrS_2.

(c) *Thermo-e.m.f.'s*

For the measurement of thermo-e.m.f. the samples were pressed into small disks $\frac{1}{4}$ in. diameter and about $\frac{1}{16}$ to $\frac{1}{8}$ in. thick, using pressures of 100,000 lb/in^2. The disks were clamped between platinum contacts, one of which could be heated electrically and the other cooled, if necessary, by a flow of water. Temperatures were measured by thermometers inserted into each contact. The e.m.f. was measured by means of a vacuum-tube voltmeter, using a Mullard ME 1400 electrometer tube followed by a D.C. amplifier. The input resistance to the electrometer tube was approximately 10^8 Ω.

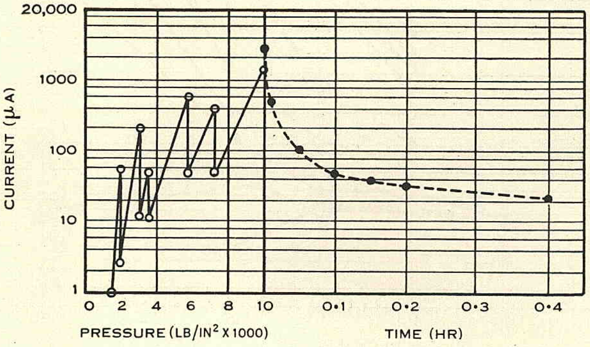

Fig. 3.—Effect of pressure increments on the conductivity of partially oxidized ZrS_2 (left-hand side) and of time (right-hand side).

It was not possible to determine unequivocally the thermo-e.m.f.'s of the four compounds having the highest resistivities, namely, HfS_3, HfS_2, $ThS_{2\cdot5}$, and ThS_2. This was in part due to the fact that a change of resistance occurred when the disks were heated and this change of input resistance affected the electrometer tube. It is likely that these four compounds are N-type semiconductors.

The thermo-e.m.f. values are included in Table 1; positive values indicate electrons flowing from platinum to chalcogenide at the hot junction, that is, N-type semiconduction.

(*d*) *Rectification*

Many of the compounds have such high resistivities that front-to-back ratios cannot be measured satisfactorily. Others undergo such rapid surface oxidation that when probes are placed on their surfaces they appear practically insulating. Tests were made for point contact rectification on certain of the materials, using both platinum and tungsten wires etched to fine points.

None of the lower chalcogenides, which were prepared as fine powders and therefore had to be pressed into disks prior to testing, showed any rectifying properties. The remainder can be divided into three classes:

(i) Those grown as single crystals, namely, TiS_3, $ZrTe_3$, and $TiTe_2$. Of these, only TiS_3 showed front-to-back ratios of about 2 : 1 at certain places.

(ii) Materials prepared as crystalline adherent masses. The only ones that exhibited rectification were $TiSe_2$, 1·2 : 1·0, and $ZrSe_3$, 2 : 1.

(iii) Finely crystalline materials produced by degradation of higher chalcogenides—these were compacted prior to testing. Only TiS_2 and $ZrSe_2$ gave front-to-back ratios of about 1·5 : 1.

In all cases the highest resistance resulted when the " whisker " was negative with respect to the chalcogenide. The results indicate no pronounced rectifying properties in this group of materials. The best examples are somewhat analogous to molybdenite in this respect without reaching the efficiency of this compound.

IV. DISCUSSION

(*a*) *Specific Resistivities*

The graphical representation (Fig. 1) of the Sp.K. values demonstrates the following interesting trends:

(i) The increasingly metallic nature of the compounds as one passes from sulphides through selenides to tellurides; the last named, except for $ThTe_{2\cdot5}$, are closely akin to alloys.

(ii) In general, for each Group IV element there is an increasingly metallic tendency as one passes from a higher to a lower chalcogenide.

(iii) The decreasingly metallic, or increasingly saltlike, nature of the compounds from Ti to Zr and Hf and finally Th is evident. It has become customary to define metallic conductivity as being shown by substances having a Sp.K. $<0\cdot01\ \Omega$cm; semiconduction by substances having Sp.K. values from 0·01 to $10^9\ \Omega$cm and insulating properties if the value is above $10^9\ \Omega$cm. If this somewhat arbitrary definition is accepted, then, taking the disulphides as an example, we have a sequence from metallic for TiS_2, through semiconduction in ZrS_2, to an Sp.K. value for HfS_2 at the extreme end of the semiconduction range, and finally a value of 10^{10} Ωcm for ThS_2, which could therefore be classed as an insulator.

For the tri- and di-compounds, it is possible to construct a useful graphical chart which expresses this sequence of increasingly saltlike characteristics of the compounds, as one passed from titanium to thorium. Such an arrangement is shown in Table 2, in which the compounds $ThS_{2\cdot5}$, $ThSe_{2\cdot5}$, and $ThTe_{2\cdot5}$ are included with the tri-compounds of the other metals. Here, the criterion for an insulator (Sp.K. $>10^9$ Ωcm) has been used for classifying the compounds as " saltlike ".

TABLE 2

TYPE OF CONDUCTION FOR THE TRI- AND DICHALCOGENIDES

Element	Sulphide		Selenide		Telluride	
	Tri or Poly	Di	Tri or Poly	Di	Tri or Poly	Di
Titanium ..	Semi	Metallic	—	Metallic	—	Metallic
Zirconium ..	Semi	Semi	Semi	Semi	Metallic	Metallic
Hafnium ..	Salt	Salt	Semi	Semi	—	—
Thorium.. ..	Salt	Salt	Semi	Semi	Semi	Semi

Some comparisons of interest are not possible, owing to the failure of titanium and hafnium to form certain tri-compounds.

The flattening of some of the curves between the compositions $AX_{1\cdot0}$ and $AX_{1\cdot5}$, especially noticeable for the Ti-Se, Ti-Te, Zr-Se, and Zr-Te systems, may be related to the manner in which the lower chalcogenides in these systems undergo transition. In these compounds there is an interpolation of additional metal atoms into vacant octahedral positions which exist between neighbouring planes of chalcogen atoms as one proceeds towards mono-compounds. Thus entirely different structures are not involved.

It will be seen that in the Th-S and Th-Se systems, the maximum value of Sp.K. occurs for the dichalcogenide. Thorium is the most basic of the four metals and forms compounds which are more stable and saltlike than the corresponding compounds of titanium etc., as may be shown by such examples as (1) the occurrence of stable thorium salts of the oxy acids sulphuric, nitric, etc., (2) the progressively increasing melting points of the tetrahalides ($TiCl_4$, −23 °C ; $ZrCl_4$, sub 331 °C ; $ThCl_4$, 765 °C), and (3) the fact that ThS_2 does not undergo degradation on heating up to m.p. 1900 °C. Hence it may be expected that the disulphide of thorium, and to a lesser extent the diselenide, are compounds of increased stability in which thorium is exerting its normal valence of four

On the other hand, any compound containing more sulphur (or selenium) than the di-compound might be expected to have a higher resistivity as is observed for HfS_2, HfS_3, etc.

Although the difference between the measured values of resistivity for TiS_3 single crystals and TiS_3 in the form of compressed powder may be due to lack of intimate contact because of air pockets etc. between particles of the powder, it is possible that the Sp.K. for the single crystals is different along different axes. This possibility is being investigated.

The Th-S and Hf-S systems appear anomalous in that the resistivity values for the lower sulphides of thorium lie below those for the corresponding compounds of hafnium. The same is true of the lower selenides of these metals. However, the magnitudes of the differences are of doubtful significance (except, perhaps, the case of $ThS_{1\cdot5}$ and $HfS_{1\cdot5}$) and the effect is not shown elsewhere.

The system Th-Te merits some comment as it yields the only sample of a " poly " telluride with an *increasing* resistivity. No satisfactory explanation can yet be suggested for this. If a small percentage of metallic tellurium is added to $ThTe_{2\cdot5}$ and the two are mixed by thorough grinding, the resistivity of the product is found to be lower than that of $ThTe_{2\cdot5}$, as would be expected because the Sp.K. of Te is approximately $0\cdot02$ Ωcm. However, for compositions containing tellurium in excess of that represented by $ThTe_{2\cdot5}$, which by X-ray analysis show the presence of free tellurium, the resistivity rises progressively with tellurium content until $Te:Th=3:1$, at which the value is 2000 Ωcm. This phenomenon appears to be associated with the fact that it is difficult to remove the excess tellurium from such materials—heating for more than a week at 600 °C was required to establish a composition $ThTe_{2\cdot5}$. Similar behaviour was found for thorium selenide compositions containing $Se:Th > 2\cdot5$ but in these, excess selenium would be expected to cause a rise in resistivity. All other chalcogenides could be separated from excess chalcogen readily as previously reported. Strotzer and Zumbusch (1941) reported the formation of what appeared to be loose compounds of thorium polysulphide and sulphur such as ThS_{10} (violet-brown) and Strotzer, Biltz, and Meisel (1939) thought that $ZrS_{3\cdot5}$ etc. were not merely mechanical mixtures. However, the excess sulphur was readily removed from these " compounds " either by leaching with CS_2 or by a sublimation during which the sulphur pressure was close to the theoretical for the temperature used. Whatever doubts may be cast on the evidence for the existence of such " compounds ", the phenomenon of increasing resistivity with increasing tellurium content may perhaps be regarded as evidence of a new kind to support such contentions.

Eastman *et al.* (1950), who gave no details of their method for determining specific resistivity, claimed that the values for the lower thorium sulphides are all below 10^{-3} Ωcm, namely, Th_7S_{12} and Th_2S_3, 10^{-3} to 10^{-4} Ωcm, $ThS < 10^{-4}$ Ωcm. These values appear very low, that for ThS approaching the value for pure thorium metal. As these workers failed to melt ThS it must be assumed that the resistivity measurement was made on a powdered sample. In the other cases their figures may refer to melted materials, which would be expected to yield lower values than powders, but scarcely of the order of 10^5 to 10^7 lower. Unfortunately, the materials referred to contained considerable amounts of impurities, the effects of which it is difficult to assess.

(*b*) *Type of Conductivity*

Except for the tri- and disulphides of titanium the compounds of this element are all metallic. Zirconium exhibits metallic conductivity in the monoselenide and monosulphide, and all telluride compounds. Hafnium closely resembles zirconium. For thorium the mono-compounds are metallic but the highest telluride is semiconducting. For hafnium and thorium the two highest sulphides, although semiconducting, have resistivities high enough for them to be regarded almost as insulators. In general, therefore, the increase in saltlike properties from titanium to thorium is again evident, as is the increase in metallic nature from sulphur to tellurium.

(*c*) *Thermo-e.m.f.*

The higher sulphides of titanium and zirconium and the two higher selenides of zirconium are N-type semiconductors with large thermo-e.m.f.'s. With hafnium, however, a fundamental change takes place and the triselenide is a P-type semiconductor with a thermo-e.m.f. of magnitude similar to those of the sulphides. From $HfSe_3$ to $HfSe_2$ there is a change from P type to N type, but in the Th-Se system the P type extends also to $ThSe_2$ and the transition to N type occurs at $ThSe_{1\cdot7}$. P-type semiconduction appears, therefore, only with the higher selenides of the more basic metals. It is possible that there are traces of free selenium in $HfSe_3$ and $ThSe_{2\cdot5}$ but this is unlikely in $ThSe_{2\cdot0}$. The analytical data are not sufficiently accurate to determine if these selenides contain a stoicheiometric excess of selenium, and further crystallographic structure data are being accumulated.

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