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

I. PREPARATION AND CHARACTERIZATION

By F. K. McTaggart and A. D. Wadsley

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[*Manuscript received May* 15, 1958]

Summary

The nine systems Ti-S, Ti-Se, Ti-Te, Zr-S, Zr-Se, Zr-Te, Hf-S, Hf-Se, and Hf-Te have been investigated by X-ray techniques for the occurrence of phases between the compositions $AX_{\mathrm{max.}}$ and AX. Compounds were prepared from materials of high purity by direct synthesis from the elements, or by degradation of a higher to a lower phase. All manipulation was done in dry argon. Several new compounds are reported, some major differences in the type of phase formed by zirconium and hafnium are noted, and a different interpretation of the X-ray data for the AX_3 compounds is discussed.

I. Introduction

We have for some time been interested in the chemistry, structure, properties, and stoicheiometry of the sulphides, selenides, and tellurides (that is, the chalcogenides) of the Group IV metals Ti, Zr, Hf, and Th. Whilst a number of combinations of these metals with the chalcogens were synthesized by early workers, it was not until the use of vapour pressure isotherms and X-ray diffraction analysis that such systems could be properly defined. However, an examination of the recent literature has disclosed many inconsistencies. There are gaps in the knowledge of the phases present in some systems and where data exist there are often considerable differences of opinion. As recently as September 1957, during the writing of this paper, Hahn and Ness (1957*a*) in reporting the Zr-Se and Zr-Te systems, apparently overlooked the fact, as others have done, that the crystals of the AX_3 compounds usually exist in the twinned form. A study of the modes of preparation of, materials used in, and chemical analyses of the compounds which have been described also led us to believe that as a preliminary to more particular studies, a general reappraisal of the systems was desirable.

The present paper discusses the preparation, analysis, and description of phases at certain fixed points in what now appear to be systems containing several non-stoicheiometric phase regions, but no attempt has been made accurately to define composition limits. Additional papers will appear in which chemical and physical properties will be described in more detail.

Data for the thorium chalcogenides will be the subject of a separate paper.

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II. EXPERIMENTAL

(a) *Materials*

The sulphur, selenium, and tellurium which were B.D.H. laboratory grade were purified by distillation, the last two under vacuum, and the first and last fractions were discarded. Titanium and zirconium metals of 99·6 and 99·8 per cent. purity, kindly made available to us by the U.S. Bureau of Mines, were reduced to filings of −150 mesh, carefully freed from iron, degreased in light petroleum, and washed with dilute acid. Hafnium metal in powder form was the best commercial grade available and contained not less than 99·5 per cent. hafnium together with approximately 0·5 per cent. zirconium.

(b) *Methods of Preparation*

(i) To prepare the higher chalcogenides provision was made for separately heating the reactants by suitable design of the vessel. For quantities up to 100 g the metal was evenly spread out in shallow silica boats placed in clear silica tubes to which an additional limb containing an excess of the non-metal was sealed at an angle of about 20°. For smaller quantities a different type of reaction tube, illustrated by Figure 1, was used. In both cases the tubes were sealed after outgassing to 0·0002 mm or better, the metal was thoroughly heated and the non-metal fused. The portion of the tube containing the metal was then heated to the desired temperature fairly rapidly, but the temperature of the non-metal was raised slowly until reaction was initiated and the rate of reaction was controlled by adjusting this temperature. Finally, the temperature of the chalcogen was brought to a value such that the pressure inside was approximately atmospheric and the tubes were then left for several weeks. Excess chalcogen was then sublimed away from the reaction products by heating to 350°C for sulphides, 450°C for selenides, and 550°C for tellurides with the other end of the tube at room temperature.

(ii) Direct reaction between accurately weighed quantities of both elements in synthesis tubes of the second type was the preferred method for synthesis of compounds containing less than the maximum non-metal–metal ratio. After degassing, the sealed evacuated tubes were heated slowly (6 hr to 2 days) and homogeneously to the desired temperature and then held for 5 to 7 days. The contents were then ground and reheated for a similar period. Additional grinding and heating cycles were made, if necessary, until equilibrium was reached. We preferred heating for long periods at a relatively low temperature in order to prevent diffusion of oxygen through the silica, which at high temperatures can result in oxidation of the chalcogenide.

(iii) Degradation, the decomposition of a higher chalcogenide to a lower one, was carried out in long clear silica tubes evacuated and sealed after careful outgassing. The end containing the charge was slowly raised to temperature whilst the other was held at room temperature. The decomposition was complete when no further sublimation occurred and this could be checked by pulling the tube an inch or so further out of the furnace and inspecting after a suitable interval for newly formed sublimate. If the composition of the original charge was known, the weights of sublimate and residual chalcogenide gave an accurate indication of the composition of the latter, and no further chemical analysis was considered necessary.

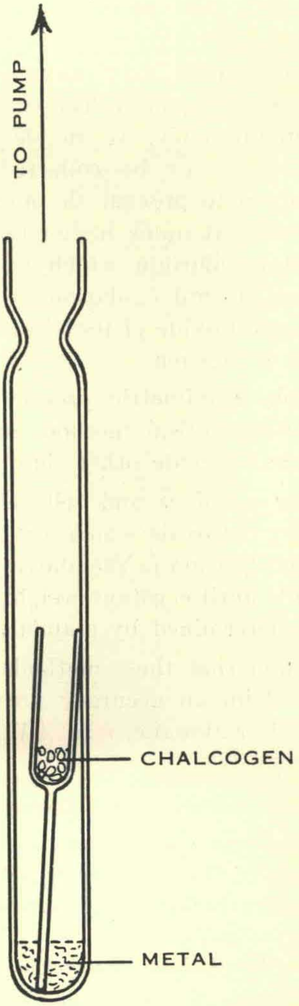

Fig. 1.—Reaction tube.

(c) *Storage and Handling*

Most of the compounds undergo oxidation to a greater or lesser extent in air. The AX compounds are usually the most reactive, TiTe for example, being pyrophoric. Of the AX_2 phases ZrS_2 can absorb up to $0 \cdot 5$ per cent. by weight of oxygen, and even the trichalcogenides AX_3 undergo some change on long exposure. All preparations were therefore manipulated and stored in an atmosphere of dry argon.

(*d*) *Methods of Chemical Analysis*

(i) *Sulphur, Selenium, and Tellurium.*—Sulphur analyses were done for us by Dr. W. Zimmermann* using the potassium fusion method developed by him (Zimmermann 1943, 1946, 1950, 1952) as a microanalytical method for materials of a widely differing nature. In contrast to many older techniques the extraction of sulphur is complete. The method is readily applicable to selenides and tellurides also.

These latter compounds may however be analysed for selenium and tellurium in the following manner: The compound is oxidized to SeO_2 or TeO_2 together with the metal oxide, at an elevated temperature. SeO_2 sublimes above about 320°C and can be collected and weighed directly providing precautions are observed to prevent the access of moisture. TeO_2 which does not sublime readily even at much higher temperatures is reduced by hydrogen at 700°C to elemental tellurium which then sublimes and may be weighed directly. In this case several oxidation-reduction cycles may be necessary to free completely the metal oxide of its tellurium content. The oxidations in all cases are carried out in oxygen.

These two simple gravimetric procedures yielded results comparable in accuracy to the microanalytical method and were frequently used when the total analysis of a chalcogenide other than a sulphide was desired.

(ii) *Metals.*—For selenides and tellurides the metal content was usually estimated by weighing the oxide which was left after selenium or tellurium had been removed by volatilization in the above gravimetric procedure. The oxides were heated to 1000°C until constant weight was achieved. The metal content of all sulphides was determined by standard wet-way analytical methods.

In spite of the fact that these methods of analysis have been found most reliable, we do not claim an accuracy greater than $\pm 0 \cdot 1$ per cent. for any component, and atomic ratios (i.e. n in AX_n) are therefore not quoted to closer than $\pm 0 \cdot 05$.

(*e*) *Density*

Densities were determined by means of a pyknometer. The quantity of chalcogenide used was of the order of $0 \cdot 5$ g and this was pumped to approximately $0 \cdot 1$ mm pressure before being covered by toluene.

(*f*) *X-Ray Diffraction Examination*

All preparations were first examined by powder diffraction methods using a camera $14 \cdot 4$ cm in diameter, the film in the asymmetric position, and CuK_α radiation. The specimens were sealed into thin-walled Lindmann glass capillaries to prevent any possible oxidation during exposure. Where the diffraction patterns could be unambiguously indexed, the unit cell dimensions were determined by the extrapolation procedure of Taylor and Floyd (1950).

The symmetry and the approximate unit cell dimensions of those trichalcogenides which formed suitable crystals were found by Weissenberg and

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precession photography with Cu and Mo radiation respectively. More accurate dimensions were then determined from films exposed in a Guinier-type focusing camera.

III. Results and Discussion

(a) *The Trichalcogenides* AX_3

Table 1 summarizes the properties of the phases of formula AX_3 which were obtained.

Titanium forms a trisulphide below 560°C and a temperature of 480–500°C was normally used during preparation. When the metal is held at a temperature higher than 560°C, TiS_2 is formed. However in both cases filamentary ribbonlike crystals of the trisulphide, up to 1½ cm long, 0·5 mm wide, and 0·01 mm thick will form by sublimation in a region of the synthesis tube where the temperature is about 460°C. Biltz, Ehrlich, and Meisel (1937) first reported the TiS_3 phase. Our sublimed crystals (Plate 1) are apparently similar to those recently described by Hahn and Harder (1956). Despite a wide range of experimental conditions, no $TiSe_3$ or $TiTe_3$ could be prepared.

Zirconium readily formed all three trichalcogenides as crystals large enough for manipulation. The trisulphide formed at 600°C and when the temperature was raised to 700°C a crystalline sublimate slowly appeared on the cooler parts of the tube. These were much smaller than the TiS_3 crystals and resembled those reported by Strotzer, Biltz, and Meisel (1940). Hägg and Schönberg (1954) who were unable to prepare either TiS_3 or ZrS_3 appear to have used too high a temperature, but Hahn *et al.* (1957) confirmed this phase.

$ZrSe_3$ and $ZrTe_3$ were formed by heating the synthesis tubes homogeneously at 600°C. Unlike $ZrSe_3$, $ZrTe_3$ sublimed readily at 800°C. Hahn and Ness (1957*a*) recently reported these two phases.

HfS_3 formed as a fine powder when the metal was held at 570–600°C and the sulphur at 420–440°C. By increasing the temperature of the chalcogenide to 800°C and heating for several months, a small quantity of crystals sublimed. $HfSe_3$ was prepared only as a finely divided powder by heating the entire tube at 600°C. No $HfTe_3$ could be made.

The crystallographic data are given in Table 1. All the trichalcogenides are isomorphous with monoclinic symmetry, and where single crystal data could be obtained it was clear that the crystals of each compound were twinned on the (001) face. Since the only systematic absences were for $(0k0)$ with $k\neq 2n$ the space group was limited to $P2_1$ or $P2_1/m$. Hahn and Harder (1956) also gave this space group for TiS_3 and Hahn and Ness (1957*a*) showed the isomorphous relationships so far as the zirconium trichalcogenides were concerned. These authors gave $(00l)$ with $l\neq 2n$ as absent spectra which, however, are not required by this space group. They also gave *c*-axis dimensions which were twice our values, and evidently overlooked the possibility of twinning in their X-ray studies. The single crystal films of our AX_3 compounds invariably showed two sets of data arising from crystals of more or less unequal size twinned on the (001) face. The only other compound which bears any resemblance to these is

TABLE 1

CHEMICAL AND CRYSTALLOGRAPHIC DATA FOR THE TRICHALCOGENIDES AX_3

Compound	Composition					Appearance	Density ($g\ cm^{-3}$)		Crystal System	Unit Cell Dimensions (Å)				Space Group
	Theoretical		Observed											
	%*A*	%*X*	%*A*	%*X*	*n*		Obs.	Calc.		*a*	*b*	*c*		
TiS_3	32·24	66·76	33·5	66·3	2·95	Bluish black filamentous ribbons	3·22	3·25	Monoclinic	5·01	3·40	8·80	98·4°	$P2_1$ or $P2_1/m$
ZrS_3	48·66	51·34	49·1	50·7	2·95	Dark orange needles	3·78	3·82	,,	5·04	3·60	8·95	98·5°	,,
$ZrSe_3$	27·80	72·20	27·3	72·8	3·05	Purplish black ribbons	5·70	5·72	,,	5·42	3·74	9·45	98·2°	,,
$ZrTe_3$	19·24	80·76	19·6	79·3	2·90	Lustrous black needles	6·80	6·82	,,	5·89	3·93	10·10	98·4°	,,
HfS_3	64·99	35·01	65·5	35·0	3·00	Bright light orange powder	*	5·70	,,	5·08	3·58	8·96	98·4°	,,
$HfSe_3$	42·99	57·01	43·1	55·5	2·90	Purplish black powder	*	7·30	,,	5·48	3·72	9·47	98·3°	,,

* Insufficient material for accurate density measurements.

uranium triselenide described by Khodad and Flahaut (1957). A literature search failed to classify this group with any AX_3 compound for which the structure is known, and the atomic arrangement of $ZrTe_3$, at present in progress, will be reported in due course.

(*b*) *The Dichalcogenides* AX_2

Table 2 summarizes the methods of formation of the dichalcogenides together with chemical analyses and crystallographic constants. Each compound crystallizes in the hexagonal system, and whilst no structure factors have been calculated all obviously have the cadmium iodide structure (Strukturbericht classification *C6*). The new compounds recorded in Table 2 are HfS_2 and $HfSe_2$. The unit cell dimensions of the remainder are in good agreement with those given by previous workers.

A feature of the preparation of $TiTe_2$ was the readiness with which sublimation took place if the temperature of the metal end of the synthesis tube was allowed to rise above about 650°C. After a few days at 750°C the entire contents of a boat would sublime away.

$HfTe_2$ could not be prepared. Mixtures of the elements in the atomic ratio 1:2 after prolonged heating gave diffraction patterns of the *B8* type with additional tellurium lines. The removal of excess non-metal gave the upper composition limit of about $HfTe_{1\cdot6}$; this is reported in the next group.

Discrepancies between the observed and calculated densities led Ehrlich (1949) to suppose that whilst $TiSe_2$ and $TiTe_2$ were ostensibly stoicheiometric, the lattices in fact had equal numbers of vacancies of both elements and therefore still gave a formula AX_2. Our data do not support this view. On the other hand a formula $Zr_{1\cdot12}Te_{1\cdot90}$, which requires an excess of metal and a deficit of tellurium, leads to better agreement between densities for the substance $ZrTe_{1\cdot7}$, which resulted from the degradation of $ZrTe_3$ at 900°C. Possibly, therefore, at the stoicheiometric limit AX_2, the lattices of the *C6* type are quite regular, and for the intermediate compositions which can extend to $AX_{1\cdot7}$ or lower, additional metal ions, absent non-metal ions or both, may be found. We believe that the type of defect which is responsible is governed by the conditions of formation and that an extended thermal investigation, beyond our present interests, must eventually be made.

(*c*) *The Sesquichalcogenides*

All compounds in this group were prepared by direct interaction of the elements at 800°C, and the only ones hitherto unreported are the hafnium compounds.

The close similarities of structure found for both the AX_3 and the AX_2 groups are not found in the sesquichalcogenides (Table 3). Ti_2Se_3, Ti_2Te_3, Zr_2Te_3, Hf_2S_3, and Hf_2Te_3 all have hexagonal symmetry and are intermediate in structure between the *C6* and *B8* types. A model in which additional metal atoms randomly occupy the octahedral positions existing between adjacent non-metal sheets of the *C6* structure has been proposed for many of the sesquichalcogenide systems (Téngner 1938). These "phases" may then be

TABLE 2

CHEMICAL AND CRYSTALLOGRAPHIC DATA FOR THE DICHALCOGENIDES AX_2

Compound	Method of Preparation	Composition					Appearance	Density (g cm^{-3})		Symmetry	Unit Cell Dimensions (Å)	
		Theoretical		Observed								
		%A	%X	%A	%X	n		Obs.	Calc.		a	c
TiS_2	Degradation of TiS_3 at 600 °C	42·75	57·25	43·4	56·5	1·95	Dark bronze	3·24	3·28	Hexagonal	3·39	5·70
$TiSe_2$	Interaction of elements 550–580 °C	23·27	76·73	23·3	76·5	2·00	Purplish brown crystals	5·26	5·26	,,	3·535	6·004
$TiTe_2$	Interaction of elements 580–620 °C	15·80	84·20	15·9	84·0	2·00	Black hexagonal plates	6·28	6·34	,,	3·76	6·48
ZrS_2	Degradation of ZrS_3 at 900 °C	58·72	41·28	58·8	40·9	2·00	Violet-brown	3·79	3·82	,,	3·662	5·813
$ZrSe_2$	Degradation of $ZrSe_3$ at 900 °C	36·61	63·34	36·9	63·0	1·95	Dark purplish brown	5·48	5·48	,,	3·770	6·137
$ZrTe_2$	Degradation of $ZrTe_3$ at 900 °C	26·33	73·67	29·4	70·5	1·70	Purplish brown	6·38	6·36†	,,	3·952	6·660
HfS_2	Degradation of HfS_3 at 900 °C	73·58	26·42	73·5	26·2	2·00	Light purplish brown	*	6·03	,,	3·635	5·837
$HfSe_2$	Degradation of $HfSe_3$ at 900 °C	53·07	46·93	54·0	44·2	1·85	Very dark brown	*	7·46‡	,,	3·748	6·159

* Insufficient material available for accurate density determinations.

† Calculated for the formula $Zr_{1\cdot12}Te_{1\cdot90}$ (see text).

‡ Calculated for $HfSe_2$ in view of analytical uncertainty.

TABLE 3

CHEMICAL AND CRYSTALLOGRAPHIC DATA FOR THE " SESQUICHALCOGENIDES " A_2X_3

Compound	Appearance	Density (g cm^{-3})		Unit Cell Formula	Symmetry	Unit Cell Dimensions (Å)		Space Group	Structure Type
		Obs.	Calc.			*a*	*c*		
Ti_2S_3	Black	3·64	3·71	$Ti_{2\cdot67}S_4$	Hexagonal	3·43	11·42	$P6_3mc$	New
Ti_2Se_3	Black	5·29	5·48	$Ti_{1\cdot33}Se_2$	,,	3·595	5·994	—	*C6–B8*
Ti_2Te_3	Black	6·30	6·40	$Ti_{1\cdot33}Te_2$	,,	3·878	6·350	—	*C6–B8*
Zr_2S_3	Black	4·29	4·29	$Zr_{20}S_{30}$	Cubic	10·253		$P4_132$ or $P4_332$	Defective NaCl
Zr_2Se_3	Black	—	6·11	Zr_4Se_6	Hexagonal	3·757	18·63	—	New
Zr_2Te_3	Black	6·40	6·40†	$Zr_{1\cdot26}Te_{1\cdot90}$	,,	3·982	6·700	—	*C6–B8*
Hf_2S_3	Light yellow-brown	*	7·50	$Hf_{1\cdot33}S_2$	,,	3·635	5·839	—	*C6–B8*
Hf_2Se_3	Black	*	Complex diffraction pattern could not be indexed						
Hf_2Te_3	Black	*	9·14	$Hf_{1\cdot33}Te_2$	Hexagonal	3·947	6·635	—	*C6–B8*

* Insufficient material for accurate density determinations.

† Based on the assumption of a defective anion lattice.

TABLE 4

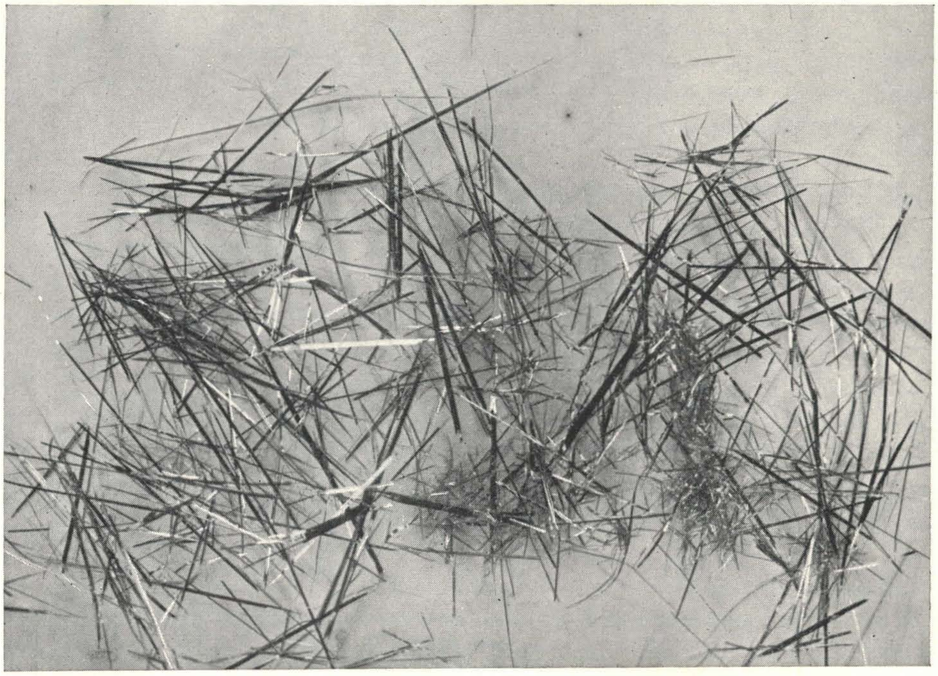
CHEMICAL AND CRYSTALLOGRAPHIC DATA FOR THE MONOCHALCOGENIDES AX

Compound	Appearance	Density (g cm^{-3})		Unit Cell Dimensions (Å)		Symmetry	Remarks
		Obs.	Calc.				
TiS	Dark grey powder	4·2	4·46	$a=3\cdot41$	$c=26\cdot41$	Hexagonal	In agreement with Hahn and Harder (1956)
				$a=9\cdot021$	$\alpha=21°\ 48'$	Rhombohedral	
TiSe	Black powder	5·7	6·34	$a=7\cdot15$	$c=12\cdot00$	Hexagonal	Dimensions from Hahn and Ness (1957*b*)
TiTe	,, ,,	6·4	7·14	$a=7\cdot72$	$c=12\cdot65$	Hexagonal	Dimensions from Hahn and Ness (1957*b*); pyrophoric
ZrS	,, ,,	4·6	4·56†	$a=10\cdot25$		Cubic	
ZrSe	Dark brown powder	5·9					Absorbs oxygen rapidly. Present data gave a mixture of $Zr+ZrSe_2$
ZrTe	Black powder	6·6	6·48	$a=3\cdot95$	$c=6\cdot64$	Hexagonal	In agreement with Hahn and Ness (1957*a*); pyrophoric
HfS	,, ,,	*					Takes up oxygen rapidly
HfSe	,, ,,	*					
HfTe	,, ,,	*					

* Insufficient material for density determinations.

† Based upon a unit cell $Zr_{24}S_{24}$.

TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM CHALCOGENIDES. I



Sublimed crystals of TiS_3(× 2).

reactive nature of these substances, the densities may not be very reliable. ZrS was reported by Hägg and Schönberg (1954) as having the tetragonal *B11* structure. We found evidence only for a cubic form which, like " Zr_2S_3 ", is based upon the NaCl-type lattice and with a quarter of each of the lattice components missing. Several diffraction lines in addition to those reported by Hahn *et al.* (1957) were recorded, requiring a unit cell size twice their value. It is probable that this corresponds to the ordering of the empty sites.

Despite numerous heat treatments, compositions designed to yield ZrSe gave mixtures of unreacted metal and a phase resembling $ZrSe_2$ rather than Zr_2Se_3 which might have been expected. ZrTe on the other hand had the *B8* structure in agreement with Hahn and Ness (1957*a*).

The diffraction pattern of HfS was quite different from that of ZrS and whilst orthorhombic indices could be assigned both to it and to HfSe we have preferred not to quote the unit cells from which they were derived, uncertain as we are of their reliability.

(*e*) *Stoichiometry*

A number of the phases we prepared had been previously described in the literature as variable in composition, and it has been customary to assign to them decimal formulae based on chemical analytical results. Biltz, Ehrlich, and Meisel (1937) gave the formula of their titanium trisulphide as $TiS_{2\cdot96}$, and Strotzer, Biltz, and Meisel (1940) consistently quote n values in ZrS_n to three places of decimals, their zirconium trisulphide, for example, being given the formula $ZrS_{2\cdot912}$.

It is recognized among analysts that sulphur determinations by methods involving roasting in air or oxygen and the subsequent estimation of the SO_2 are by no means reliable. The main difficulty is to free the metal oxide from the last traces of sulphur. Such a technique was the one largely adopted by Biltz and his coworkers, and it is a matter for surprise to find formulae quoted to a degree of accuracy which neither the method nor the results of their analyses could justify. An error of 0·1 per cent. in the analysis of both components in TiS_3—which may be expected even when using the most refined techniques—can lead to extremes of formula $TiS_{2\cdot984}$ and $TiS_{3\cdot016}$. When coupled with the impurities present in the metals an even greater degree of uncertainty in the formula must be recognized. There is little chemical evidence to suggest that the trichalcogenides are anything but stoichiometric.

In between the limits AX_2 and AX gross changes of chemical composition in a particular phase may occur which are well outside the limits of experimental error. All the dichalcogenides have a range of composition extending from AX_2 to at least $AX_{1\cdot7}$.

Most striking, perhaps, of the non-stoichiometric systems yet described, is the phase varying in composition from Zr_5S_8 to Zr_9S_8. Many of the supposedly simple oxides with the NaCl structure such as NbO, TiO and VO (reported respectively by Andersson and Magnéli 1957; Ehrlich 1939; Schönberg 1954) have a quarter of both metal and non-metal sites vacant. ZrS, on our evidence, presents an exact analogy, and the extended composition range is apparently due to the variation in the number of these sites which are occupied.

It is a matter of considerable doubt whether *AX* compounds with the *B8* structure can have a range of composition. Before finality may be reached on any particular system detailed studies of the methods of preparation and thermal history should be made and even the introduction of an order-disorder parameter should be considered.

(*f*) *Hafnium and Zirconium Chalcogenides*

In view of the very close similarity between hafnium and zirconium throughout their known chemical behaviour, it is a matter of considerable interest that the chalcogenides of these two elements may differ widely. Hafnium does not form a tri- or a ditelluride although zirconium forms both. Also the sesquisulphides and sesquiselenides of the two metals differ in structure. While in the case of the sesquiselenides the differences may simply be due to stacking imperfections, for the sesquisulphides, the differences are profound, not only in structure but also in appearance. This is a matter for further study.

IV. ACKNOWLEDGMENTS

The authors wish to express their thanks to Dr. B. Dawson for helpful discussions, and in particular for those concerning the data for the AX_3 compounds which led to the realization that twinning had occurred. They also wish to thank Miss Joy Bear for carrying out the density determinations and a number of the analyses.

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