

## On the Properties of $\text{TiS}_3$ , $\text{ZrS}_3$ , and $\text{HfS}_3$

HAAKON HARALDSEN, ARNE KJEKSHUS, ERLING RØST and  
ARNE STEFFENSEN\*

*Kjemisk Institutt A, Universitetet i Oslo, Blindern, Norway*

Tensimetric analysis of the hafnium-sulfur system is reported and discussed, particularly in relation to similar measurements on titanium, zirconium, niobium, tantalum, and uranium sulfides.

The properties of the polysulfide compounds  $\text{TiS}_3$ ,  $\text{ZrS}_3$ , and  $\text{HfS}_3$  have been studied by means of X-ray diffraction methods and magnetic susceptibility measurements.

The redetermined lattice constants are:

$\text{TiS}_3$ ,  $a = 4.973 \text{ \AA}$ ,  $b = 3.433 \text{ \AA}$ ,  $c = 8.714 \text{ \AA}$ ,  $\beta = 97.74^\circ$   
 $\text{ZrS}_3$ ,  $a = 5.123 \text{ \AA}$ ,  $b = 3.627 \text{ \AA}$ ,  $c = 8.986 \text{ \AA}$ ,  $\beta = 97.15^\circ$   
 $\text{HfS}_3$ ,  $a = 5.100 \text{ \AA}$ ,  $b = 3.594 \text{ \AA}$ ,  $c = 8.992 \text{ \AA}$ ,  $\beta = 98.16^\circ$

The compounds have almost zero magnetic susceptibility.

An interesting class of transition metal substances consist of the polychalcogenide compounds of the subgroup IV, V, and VI elements. Chromium is the only metal among these elements which has not been reported to form such compounds. The composition of these polycompounds varies from  $\text{TX}_4$  in  $\text{VS}_4^{1-3}$  to  $\text{T}_2\text{X}_5$  in  $\text{Th}_2\text{S}_5^{4-7}$  and  $\text{Th}_2\text{Se}_5^{5-8}$ . With these exceptions the common composition is  $\text{TX}_3$ , found in  $\text{TiS}_3^{5,6,9-13}$ ,  $\text{ZrS}_3^{5,6,12-15}$ ,  $\text{ZrSe}_3^{5,6,12,13,16,17}$ ,  $\text{ZrTe}_3^{5,6,12,18}$ ,  $\text{HfS}_3^{5,6,12,13}$ ,  $\text{HfSe}_3^{5,6,12}$ ,  $\text{ThTe}_3^7$ ,  $\text{NbS}_3^{19-22}$ ,  $\text{NbSe}_3^{23}$ ,  $\text{NbTe}_3^{23}$ ,  $\text{TaS}_3^{24-26}$ ,  $\text{TaSe}_3^{26}$ ,  $\text{TaTe}_3^{26}$ ,  $\text{US}_3^{27-30}$ ,  $\text{USe}_3^{30-32}$  and  $\text{UTe}_3^{30}$ . Three more  $\text{TX}_3$  compounds, *i.e.*  $\text{MoS}_3^{33}$ ,  $\text{WS}_3^{34-35}$ , and  $\text{WSe}_3^{34}$ , have been inferred from chemical analysis but their existence does not appear to be properly established. Although several investigations have been carried out to collect information on the thermodynamic (vapor pressure data), structural (mostly lattice parameter values), magnetic and electrical properties there is still some information lacking. Detailed investigations are necessary for a complete description of the chemical bonding in these compounds, but some information might, as is known from other simple cases, also be acquired from a more complete knowledge of some of the substances.

The present paper concerns the properties of  $\text{TiS}_3$ ,  $\text{ZrS}_3$ , and  $\text{HfS}_3$ .

\* Present address: Norsk Ytong A/S, Hokksund, Norway.

## EXPERIMENTAL

*Materials.* The titanium, zirconium and hafnium metals used in this study were supplied by A. D. MacKay, Inc., New York. The "iodide" titanium and zirconium were nominally 99.99 % and 99.9 % pure. A spectrographic analysis of the titanium metal showed the presence of 30 ppm of Fe and Mn and less than 10 ppm of Cu. Hafnium metal in sintered lumps contained not less than 98.5 % hafnium.

The sulfur was "Spectrographically pure sulfur" from American Smelting and Refining Co., and according to the supplied analysis it contained 99.999 % sulfur.

*Preparations.* Titaniumsulfides with composition 66.67, 71.47 and 75.00, zirconium-sulfides with 66.67, 71.47, 75.00 and 77.78, and hafniumsulfides with 66.67, 67.74, 75.00, 75.30 and 80.00 atomic % S were made. The specimens were prepared by heating accurately weighed quantities of sulfur and titanium zirconium or hafnium respectively, in evacuated and sealed silica tubes for about two days at various temperatures, ranging from 500° to 650°C. Samples containing more than 75 atomic % sulfur were heated for about a week at 400 and 300°C. To obtain a better crystallisation some samples were annealed for about one week at 600°C.

To prepare large single crystals specimens were heated in a furnace with a temperature gradient.

*Vapor pressure measurements.* The method used for vapor pressure measurements is based on the use of a Bodenstein<sup>36</sup> — Johnson<sup>37</sup> gauge of vitreous silica used as a null instrument between the hot vapor to be measured and an inert gas, the pressure of the latter being measured on a conventional mercury manometer. A detailed description of the apparatus and its most important parts may be found in the literature, cf. Biltz and Juza<sup>38</sup> and Haraldsen<sup>39</sup>. The present refinements and modifications concern methods for the control and uniformity of the temperature, the accuracy of temperature-measurements, the vacuum equipment for outgassing of the apparatus and sensitivity and accuracy of the observed deflections on the null detector.

The main parts of the apparatus are the *reaction space*, the *vacuum pumps*, the *furnaces* and their *regulators* and the *temperature* and *pressure* measuring equipment. The reaction space made in vitreous silica consists of the sample container, the spiral which is surrounded by the manometer mantle, and the communication capillary joining the substance container and the spiral gauge. The capillary is, via a "sulfur-valve" and sulfur receiving tube connected to the high vacuum pumpline. High vacuum of about  $5 \times 10^{-6}$  mm Hg was obtained with an Edwards oil diffusion pump and the pressure was measured on a combined Pirani and ionisation gauge during outgassing of the apparatus.

The sample container is immersed in a steel block inside a platinum furnace whose temperature regulation is achieved by an automatically controlled autotransformer. The temperature of the sample was during each experimental run recorded on a Philips temperature recorder and the regulated temperature was not subject to variations larger than  $\pm 0.1^\circ\text{C}$ . The spiral gauge and the communication capillary were heated separately and the regulated and controlled temperature was measured in the middle of the spiral gauge and on three different places along the communication capillary. The Pt/Pt—Rh thermocouples had been calibrated with a standard couple carrying a certificate from National Bureau of Standards. The thermocouple of the substance container was furthermore separately calibrated by a melting standard sample of zinc (m.p.  $419.5_0^\circ\text{C}$  according to NBS) and at the ice point and steam point of water.

The vapor from the heated sample exerts its pressure on the spiral manometer moving the pointer from its zero position. This is detected optically with the reflected light from a mirror on the tip of the pointer. The light passes through a window of plane parallel quartz in the manometer mantle. The linearity of the spiral manometer was tested with positive as well as negative pressure differences in the range of  $\pm 500$  mm Hg. Linearity was indeed found and the sensitivity was such that a pressure of 1 mm Hg caused a deflection of 0.2 mm on a transparent scale in a distance of 300 mm from the mirror.

To test the performance of the apparatus the vapor pressure of the available spectrographically pure sulfur was determined at different temperatures. The present observed vapor pressure ( $P_{\text{obs}}$ ) are listed in Table 1 together with the corresponding values ( $P_{\text{ref}}$ ) obtained by West and Menzies<sup>40</sup>. As can be seen from Table 1 the agreement between the two sets of values is good and the results seem to be reliable within an accuracy of  $\pm 2$  mm Hg.

Table 1. Vapor pressure of sulfur at different temperatures.

$t$ (°C)	$P_{\text{obs}}$ (mm Hg)	$P_{\text{ref}}$ (mm Hg)
227.2	6.9	6.0
228.0	7.0	6.1
280.9	30.7	31.0
281.0	30.5	31.1
311.2	65.8	66.1
311.7	66.7	66.9
323.1	87.2	86.8
323.3	86.8	87.2
343.2	133.6	132.2
354.9	164.8	167.2
355.1	166.0	167.9
391.1	326.6	326.3
391.2	324.8	326.8
402.3	392.0	393.7
402.5	396.3	395.1
420.9	531.5	531.9
421.2	533.8	534.2
439.3	701.7	702.7
439.4	701.7	703.8

*X-Ray diffraction.* The X-ray photographs of the samples were taken in a Guinier focusing camera of 80 mm diameter and strictly monochromatized  $\text{CuK}\alpha_1$ -radiation.

For the calculation of lattice constants by the Guinier method potassium chloride (Analar, The British Drug Houses Ltd.  $a = 6.2919 \text{ \AA}$ <sup>41</sup>) was added as an internal standard. Lattice constants are expressed in Ångström units on the basis of  $\lambda_{\text{CuK}\alpha_1} = 1.54050 \text{ \AA}$ . Lattice constants from earlier investigations expressed in kX-units have been transformed to Å by multiplication by the factor 1.00202.

*Magnetic measurements.* The magnetic susceptibilities were measured by the Gouy method at three different maximum field strengths at  $-183$ ,  $-78$ ,  $20$ ,  $150$ , and  $300^\circ\text{C}$ . The samples were enclosed in evacuated and sealed thin-walled quartz or Pyrex tubes of about 2 mm internal diameter, and to a height of about 85 mm.

## RESULTS

*Vapor pressure measurements.* The measurements consisted of determining the pressure of sulfur in equilibrium with hafnium sulfides as a function of sulfur contents between  $\sim 80.0$  and  $66.7$  atomic % S. Only a short time was required to obtain equilibrium in the concentration range between  $80.0$  and  $75.0$  atomic % S both for increasing and decreasing temperatures, whereas equilibrium was achieved very slowly between  $75.0$  and  $66.7$  atomic % S for decreasing temperatures. As the pressure in the latter region very soon came to constant value with increasing temperature, the pressure values obtained in this way were used as equilibrium values. Hafnium sulfides with sulfur contents less than  $66.7$  atomic % S could not be examined because the dissociation pressure even at  $1.000^\circ\text{C}$  was too low to be measured.

The results of the sulfur pressure measurements at various compositions and temperatures are shown in Fig. 1. The general nature of the results resembles that obtained in other sulfide systems by Biltz and his co-workers. In the neighbourhood of the compositions  $\text{HfS}_3$  and  $\text{HfS}_2$  the rapid variation

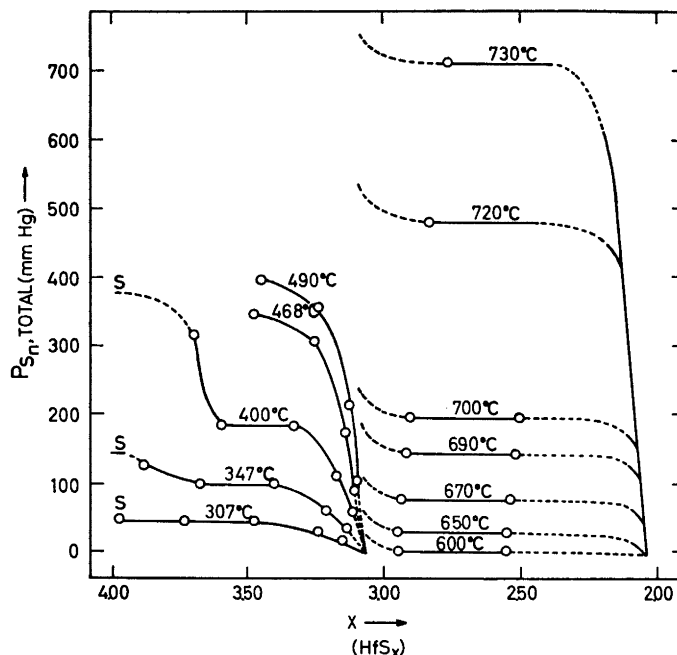
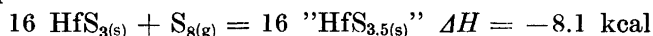


Fig. 1. Pressure-composition isotherms for the hafnium-sulfur system.

of the pressure for any given isotherm indicate the existence of two solid phases. The composition of the two phases is in agreement with the solid phases in the Hf-S system located by X-ray analysis.

In an ideal system with true stoichiometry of the phases, extended flat regions in the isotherms over broad concentration ranges and sharp breaks in a rather narrow concentration range around the composition of the phases are found. It is evident, however, that the form of the isotherms in Fig. 1 at higher concentrations of sulfur is of a peculiar shape. By inspection of the curves, the presence of a third phase might at first be suggested. Although the composition of this "phase" estimated from the first run shown in Fig. 1 closely approached  $\text{HfS}_{3.5}$ , it does not, according to the X-ray photographs resemble a crystalline phase. Other experiments carried out on new samples clearly revealed that this "phase" certainly did not have any definite composition, but that the apparent composition depends on the sample. An explanation based on the assumption that  $\text{HfS}_3$  exists over a particular wide range of compositions on the sulfur-rich side is inconsistent with the variation from sample to sample, and furthermore with the results obtained by X-ray diffraction. Having regard to the experimental details the most probable explanation seems to be that sulfur is adsorbed on the surface of  $\text{HfS}_3$ , *cf.* Bear and McTaggart<sup>5</sup>. The form of the isotherms resembles that of absorption isotherms and the main features are similar to the curves representing for example the amount of hydrogen taken up by palladium at various pressures and tempera-

tures. The heat of adsorption calculated according to the plateaus found in the first run



is of the order of magnitude expected for adsorption.

Several samples were now synthesized by heating  $\text{HfS}_3$  with variable amounts of sulfur. Up to a sulfur content indicated by  $\text{HfS}_{3.5}$  the samples appeared to be homogeneous and no free sulfur could be seen in the silica tubes. The Guinier photographs furthermore showed the presence of only one phase,  $\text{HfS}_3$ , but the lattice parameter values (see page 1290) indicate that the homogeneity range of  $\text{HfS}_3$  is rather narrow. However, by heating the samples of approximate composition of  $\text{HfS}_{3.5}$  in a furnace with a gradient the expected amounts of free sulfur and  $\text{HfS}_3$  were achieved. The same amount of free sulfur can also be removed by extraction with  $\text{CS}_2$ , see also Strotzer *et al.*<sup>14</sup>

In order to get information about the surface areas of the  $\text{HfS}_3$  samples one portion of  $\text{HfS}_3$  was measured by the BET-method. The surface of this sample was found to be  $10.1 \text{ m}^2/\text{g}$ . Judging from the diffuseness of the X-ray lines in the Guinier photographs the different samples did not differ much from this value when they were synthesized in a similar way. In order to explain the apparent formula  $\sim \text{HfS}_{3.5}$  about 0.5 gram atoms of sulfur have to be adsorbed per gram mole  $\text{HfS}_3$ . As a single layer of atomic sulfur on the surface of  $\text{HfS}_3$  would require a much greater area than that available, chains or rings of sulfur must be the molecular species present on the surface.

A further, quantitative interpretation of the sulfur vapor pressure isotherms with more than 75.0 atomic % sulfur is difficult because of two other notable properties of  $\text{HfS}_3$  (and also the isotopic tri-sulfide compounds).  $\text{HfS}_3$  is to some extent soluble in liquid sulfur which is seen from a melting point depression of about  $0.5\text{--}1.0^\circ\text{C}$  obtained in different mixtures of  $\text{HfS}_3$  in pure sulfur. Due to the uncertainties involved in the determination of the melting point of sulfur this method did not yield very precise results. Smaller discrepancies between the observed pressure and the pressure of pure sulfur at higher sulfur content may be explained in this way, whereas it is assumed that the vapor pressure depression due to the solubility of  $\text{HfS}_3$  only to a small extent governs the isotherms from  $\text{HfS}_3$  to  $\sim \text{HfS}_{3.8}$ , *cf.* Fig. 1.

The three tri-sulfides are furthermore subject to sublimation which means that molecular species of the type  $\text{HfS}_3$  or  $\text{Hf}_2\text{S}_6$  are present in the vapor phase. These molecules will also contribute to the total vapor pressure. It is nevertheless assumed that this will make only a minor correction to the sulfur pressure.

The picture outlined here as an explanation of the peculiar form of the sulfur isotherms for sulfur content higher than 75.0 atomic % S seems to apply also to the analogous transition metal sulfide systems  $\text{Zr-S}$ ,<sup>14</sup>  $\text{Nb-S}$ <sup>19</sup> and  $\text{Ta-S}$ ,<sup>24</sup> whereas the deviations are less pronounced in the  $\text{Ti-S}$ <sup>9</sup> system and furthermore the  $\text{U-S}$ <sup>27</sup> system behaves almost as an ideal system.

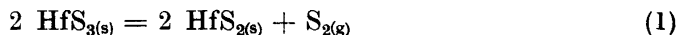
In the concentration range from  $\text{HfS}_{3.00}$  to  $\text{HfS}_{2.00}$  the recorded data are in accordance with the expected form of the isotherm in a two-phase region. The composition of the residual crystalline phase after complete degradation up to  $1000^\circ\text{C}$  was found to be  $\text{HfS}_{2.07}$  and  $\text{HfS}_{2.04}$  for two different runs. This

Table 2. Observed dissociation pressures of  $\text{HfS}_3$  ( $P_{\text{Total}}$ ) and calculated partial pressures ( $p_{\text{S}_2}$ ) at different temperatures.

$T$ ( $^{\circ}\text{K}$ )	$P_{\text{Total}}$ (mm Hg)	$p_{\text{S}_2}$ (mm Hg)
873	4	4
923	30	29
943	80	77
963	147	139
973	199	186
993	485	428
1003	717	611

result is essentially in agreement with the results obtained from the X-ray photographs showing the characteristic line pattern of the  $\text{Cd}(\text{OH})_2$ -C6-type structure of the  $\text{HfS}_2$ -phase. The lattice constant value of  $c = 5.862 \text{ \AA}$  (maximum error  $\pm 0.005 \text{ \AA}$ ) is considerably different from the value  $c = 5.837 \text{ \AA}$  given by McTaggart and Wadsley,<sup>12</sup> whereas the value  $a = 3.633 \text{ \AA}$  agrees fairly well with the previous value of  $a = 3.635 \text{ \AA}$ .

For an evaluation of thermodynamic data from the observed sulfur pressure the available equilibrium constants between the various kinds of gaseous sulfur  $\text{S}_2$ ,  $\text{S}_4$ ,  $\text{S}_6$ , and  $\text{S}_8$  by Braune *et al.*<sup>42</sup> have been used to calculate the partial pressure of  $\text{S}_2$ . The total dissociation pressure of  $\text{HfS}_3$  and the obtained partial pressure of diatomic sulfur at various temperatures are listed in Table 2 for:



The estimation of the partial pressures of  $\text{S}_2$  for the dissociation of the analogous compounds,  $\text{TiS}_3$  and  $\text{ZrS}_3$  was originally based by Biltz and co-

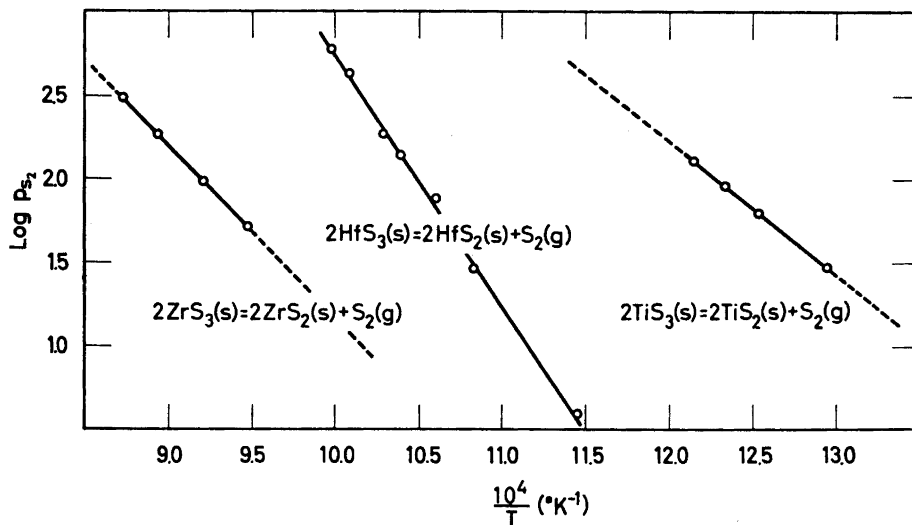


Fig. 2. van't Hoff plots for the thermal decomposition of  $\text{TiS}_3$ ,  $\text{ZrS}_3$ , and  $\text{HfS}_3$ .

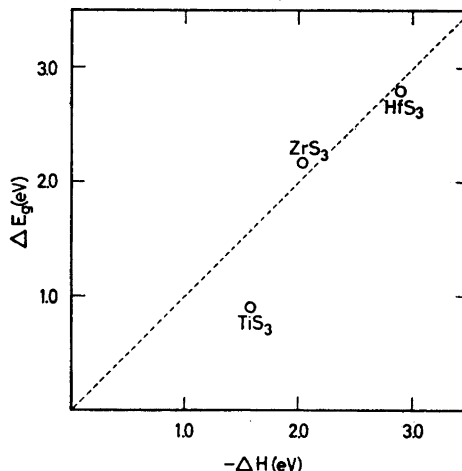
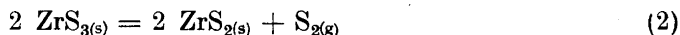
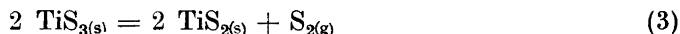


Fig. 3. Empirical relationship [between the energy gap  $\Delta E_g$  and the heat of formation  $\Delta H$ . The broken line indicates  $\Delta E_g = 1 - \Delta H$ .

workers on the work by Preuner and Schupp<sup>43</sup>. This work has since been shown to be considerably erroneous by Klemm and Kilian<sup>44</sup> and Braune *et al.*<sup>42</sup> and a re-evaluation of these data has therefore also been made for comparison. The data for the vapor pressure of



give, after this recalculation,  $p_s$  values of 52, 97, 185, and 307 mm Hg at 1056, 1087, 1120, and 1147°K, respectively. For the reaction



$p_s$  is found to be equal to 30, 62, 90, and 127 mm Hg at 773, 798, 811, and 824°K, respectively.

From a van't Hoff plot ( $\log p_s$  versus  $1/T$ ), *cf.* Fig. 2.  $\Delta H$  values are evaluated by taking the slope of the best straight line through the points. The obtained values for the heat of formation,  $\Delta H = -\Delta H_{\text{diss}}$ , are  $-68.0$ ,  $-47.2$  and  $-36.6$  kcal mole<sup>-1</sup> for the reactions according to eqns. 1, 2, and 3, respectively.

On the basis of the discussed relationship between the energetic, electro-physical and mechanical properties of semiconductors, *cf.* Mooser and Pearson,<sup>45</sup> it is interesting to note that the present  $\Delta H$  values (measured in eV) are closely related to the  $\Delta E_g$  values of the forbidden energy gaps (*cf.* Fig. 3) in these substances which indeed are semiconductors according to Grimmeiss *et al.*<sup>13</sup> This relationship is perhaps worth a further study in view of the chemical interpretation of the energy levels in semiconductors proposed by Ruppel *et al.*<sup>46</sup> According to Ruppel *et al.* the heat of formation from the elements,  $\Delta H_f$ , may be used as a measure for the strength of the bonds in a semiconductor, and a relationship between  $\Delta H_f$  and  $\Delta E_g$  has been proposed. Further considerations of the possible correlation between  $\Delta H$  and  $\Delta E_g$  is desirable before any definite conclusions are drawn. Nevertheless whilst waiting for these experiments to be carried out, the observed correlation should

Table 3. Guinier photograph data of  $\text{TiS}_3$ ,  $\text{ZrS}_3$  and  $\text{HfS}_3$  taken with strictly monochromatized  $\text{CuK}\alpha_1$  -radiation.

<i>hkl</i>	$\sin^2\theta \times 10^5 \quad I_{\text{obs}}$					
	$\text{TiS}_3$		$\text{ZrS}_3$		$\text{HfS}_3$	
001	780	m	745	m	749	m
100	2439	vw	2295	vw	2332	vw
10 $\bar{1}$	2859	vw	2716	w	2700	vw
002	3116	w	2989	w	2995	w
101	3595	vw	3368	w	3450	vw
011	—	—	5257	w	5333	m
003	7034	vw	—	—	6738	vw
110	—	—	6806	w	6921	w
012	8248	vst	7505	vst	7593	vst
200	—	—	9183	w	} 9312	m
20 $\bar{1}$	9805	w	9263	w		
201	11289	w	10602	w	} 10812	w
20 $\bar{2}$	11416	w	10853	w		
013	12147	vw	11231	w	} 11338	vw
210	14905	st	13703	m		
21 $\bar{1}$	14933	st	13774	m	} 13909	st
211	16427	w	15103	m		
21 $\bar{2}$	16518	w	15356	m	—	—
014	17624	vw	16471	w	16573	w
020	20501	st	18048	st	18373	st
021	21289	vw	18789	w	19114	w

Table 4. Lattice constants of  $\text{TiS}_3$ ,  $\text{ZrS}_3$  and  $\text{HfS}_3$ .

Compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	Reference
$\text{TiS}_3$	4.973	3.433	8.714	97.74	Present
	4.99	3.38	$2 \times 8.8$	97.5	Hahn and Harder <sup>10</sup>
	4.97	3.42	8.78	97.17	Jeannin and Bénard <sup>11</sup>
	5.01	3.40	8.80	98.4	McTaggart and Wadsley <sup>12</sup>
	5.01	3.40	8.80	98.4	Grimmeiss <i>et al.</i> <sup>13</sup>
$\text{ZrS}_3$	5.123	3.627	8.986	97.15	Present
	5.17	3.66	$2 \times 9.17$	98.1	Hahn <i>et al.</i> <sup>15</sup>
	5.04	3.60	8.95	98.5	McTaggart and Wadsley <sup>12</sup>
	5.04	3.60	8.95	98.5	Grimmeiss <i>et al.</i> <sup>13</sup>
$\text{HfS}_3$	5.100	3.594	8.992	98.16	Present
	5.08	3.58	8.96	98.4	McTaggart and Wadsley <sup>12</sup>
	5.08	3.58	8.96	98.4	Grimmeiss <i>et al.</i> <sup>13</sup>

be looked on as a rough rule for an estimation of either  $\Delta H$  or  $\Delta E_g$  if one of them is known.

*Crystallographic data.* Guinier photographs of  $\text{TiS}_3$ ,  $\text{ZrS}_3$ , and  $\text{HfS}_3$  were indexed on the basis of monoclinic unit cell, *cf.* Table 3. The lattice constants of the samples with composition  $\text{MeS}_3$  are found in Table 4 together with the



Table 5. Magnetic susceptibilities of TiS<sub>3</sub>, ZrS<sub>3</sub> and HfS<sub>3</sub>,  $\chi_g \times 10^6$ .

Compound	Temperature °C					Induced diamagnetism
	-183	-78	20	150	300	
TiS <sub>3</sub>	-0.09	-0.08	-0.09	-0.09	-0.09	-0.71
ZrS <sub>3</sub>	-0.18	-0.18	-0.19	-0.19	-0.19	-0.58
HfS <sub>3</sub>	-0.20	-0.20	-0.21	-0.21	-0.21	-0.41

previous lattice constant values. The lattice constants of the different compounds are found to be independent of the composition within the experimental error. Thus, the homogeneity ranges of the compounds are supposedly rather narrow. The lattice constants resemble those of the earlier investigators, *cf.* Table 4, but the earlier values differ to some extent from the values found here. No indication of the doubling of the *c*-axis reported by Hahn and co-workers<sup>10,15</sup> was found in this study. The apparent doubling is according to McTaggart and Wadsley<sup>12</sup> due to twinning of the crystals on the (001) face.

The only systematic missing reflections in the Weissenberg photographs of single crystals of ZrS<sub>3</sub> are of the type (0*k*0) when  $k = 2n + 1$ . The highest symmetric space group is thus  $P2_1/m (C_{2h}^2)$ .

The three sulfides are undoubtedly isotypic, *cf.* Table 3, but their detailed crystal structure is not known. Apparently, isotypic compounds are found among the trichalkogenides of the transition metals listed in the introduction. Structure determination of this class of compounds is limited to the reported 010-projection of ZrSe<sub>3</sub> by Krönert and Plieth<sup>16</sup>.

*Magnetic properties.* The magnetic susceptibilities of TiS<sub>3</sub>, ZrS<sub>3</sub>, and HfS<sub>3</sub> were measured at five different temperatures between -183 and 300°C. The results listed in Table 5 are mean values of the susceptibilities measured at three different field strengths ( $H_{\max} = 4015, 4700, \text{ and } 5110 \text{ Oe}$ , respectively).

The measured susceptibilities are all exceedingly low and almost balanced by the diamagnetism induced in the compounds. The diamagnetic corrections are  $-5 \times 10^{-6}$  per mole Ti<sup>4+</sup>,  $-10 \times 10^{-6}$  per mole Zr<sup>4+</sup>,  $-16 \times 10^{-6}$  per mole Hf<sup>4+</sup> according to Klemm,<sup>47</sup> and  $-32.6 \times 10^{-6}$  per mole S<sup>2-</sup> according to Angus<sup>48</sup>. The corrections are listed for one gram of the compounds in the far right column of Table 5. By subtracting these values from the measured susceptibilities the susceptibilities of the metal atoms are obtained. The effective magnetic moments which range from 0.21 to 0.64 Bohr magnetons may be said to be in agreement with all the three main models of the chemical bond.

A metallic type of bond or an ionic bond description (probably corresponding to quadrivalent metal ions, S<sub>2</sub><sup>2-</sup> groups and S<sup>2-</sup>) can supposedly be excluded by reason of the electrical conductivity measurements by McTaggart<sup>6</sup> and Grimmeiss *et al.*<sup>13</sup> The experimentally observed semiconductivities in these compounds are, however, in essential agreement with the proposed covalent valence-type of chemical bond expected in semiconductors, *cf.* Mooser and Pearson<sup>45</sup>. Further support for a covalent type of bonding is the fact that crystals of these compounds are grown from the vapor phase, probably via gaseous molecules MeS<sub>3</sub> or Me<sub>2</sub>S<sub>6</sub>.

*Acknowledgements.* The financial assistance of *Norges almenvitenskapelige forskningsråd* is gratefully acknowledged (H.H.). Two of the authors (H.H. and A.K.) also wish to thank *Norsk Hydros fond* for financial support. The authors thankfully recognize the help of civiling. Hans Bohlbro, Haldor Topsøe's Laboratory, Copenhagen, Denmark, in the surface measurements of  $\text{HfS}_2$  and cand. real. Liv Gjertsen in carrying out some of the magnetic measurements.

## REFERENCES

1. Klemm, W. and Hoschek, E. *Z. anorg. allgem. Chem.* **226** (1936) 359.
2. Biltz, W. and Köcher, A. *Z. anorg. allgem. Chem.* **242** (1939) 324.
3. Pedersen, B. *Acta Chem. Scand.* **13** (1959) 1050.
4. Strotzer, E. F. and Zumbusch, M. *Z. anorg. Chem.* **247** (1941) 415.
5. Bear, J. and McTaggart, F. K. *Australian J. Chem.* **11** (1958) 458.
6. McTaggart, F. K. *Australian J. Chem.* **11** (1958) 471.
7. Graham, J. and McTaggart, F. K. *Australian J. Chem.* **13** (1960) 67.
8. D'Eye, R. W., Sellmann, R. G. and Murray, J. R. *J. Chem. Soc.* **1952** 2555.
9. Biltz, W., Ehrlich, P. and Meisel, K. *Z. anorg. allgem. Chem.* **234** (1937) 97.
10. Hahn, H. and Harder, B. *Z. anorg. allgem. Chem.* **288** (1956) 241.
11. Jeannin, Y. and Bénard, J. *Compt. Rend.* **246** (1958) 614.
12. McTaggart, F. K. and Wadsley, A. D. *Australian J. Chem.* **11** (1958) 445.
13. Grimmeiss, H. G., Rabenau, A., Hahn, H. and Ness, P. *Z. Elektrochem.* **65** (1961) 776.
14. Strotzer, E. F., Biltz, W. and Meisel, K. *Z. anorg. allgem. Chem.* **242** (1939) 249.
15. Hahn, H., Harder, B., Mutschke, U. and Ness, P. *Z. anorg. allgem. Chem.* **292** (1957) 82.
16. Krönert, W. and Pliehl, K. *Naturwissenschaften* **45** (1958) 416.
17. Hahn, H. and Ness, P. *Z. anorg. allgem. Chem.* **302** (1959) 37.
18. Hahn, H. and Ness, P. *Z. anorg. allgem. Chem.* **302** (1959) 136.
19. Biltz, W. and Köcher, A. *Z. anorg. allgem. Chem.* **237** (1938) 369.
20. Jellinek, F., Brauer, G. and Müller, H. *Nature* **185** (1960) 376.
21. Grigorian, L. A. and Novoselova, A. V. *Dokl. Akad. Nauk SSSR* **144** (1962) 75.
22. Furuseth, S. and Kjekshus, A. *To be published.*
23. Kjekshus, A. and Selte, K. *To be published.*
24. Biltz, W. and Köcher, A. *Z. anorg. allgem. Chem.* **238** (1938) 81.
25. Jellinek, F. *J. Less-Common Metals* **4** (1962) 9.
26. Bjerkelund, E. and Kjekshus, A. *To be published.*
27. Strotzer, F., Schneider, O. and Biltz, W. *Z. anorg. allgem. Chem.* **243** (1940) 307.
28. Picon, M. and Flahaut, J. *Compt. Rend.* **244** (1957) 1777.
29. Picon, M. and Flahaut, J. *Bull. Soc. Chim. France* **1958** 772.
30. Grønvoold, F., Haraldsen, H., Thurmann-Moe, T. and Tufte, T. *To be published.*
31. Khodadad, P. and Flahaut, J. *Compt. Rend.* **244** (1957) 462.
32. Trzebiatowski, W. and Suski, W. *Bull. Acad. Polon. Sci. Ser. Sci. Chim.* **9** (1961) 277.
33. Biltz, W. and Köcher, A. *Z. anorg. allgem. Chem.* **248** (1941) 172.
34. Glemser, O., Sauer, H. and König, P. *Z. anorg. Chem.* **257** (1948) 241.
35. Ehrlich, P. *Z. anorg. Chem.* **257** (1948) 247.
36. Bodenstein, M. *Z. Elektrochem.* **14** (1908) 544; see also Bodenstein, M. and Katayana M. *Z. physik. Chem.* **69** (1909) 26.
37. Johnson, F. M. G. *Z. physik. Chem.* **61** (1908) 457.
38. Biltz, W. and Juza, R. *Z. anorg. allgem. Chem.* **190** (1930) 161.
39. Haraldsen, H. *Skrifter Norske Videnskapsakad. Oslo I. Mat. Naturv. Kl.* **1933** No. 9.
40. West, W. A. and Menzies, A. W. C. *J. Phys. Chem.* **33** (1929) 1880.
41. Hambling, P. G. *Acta. Cryst.* **6** (1953) 98.
42. Braune, H., Peter, S. and Neveling, V. *Z. Naturforsch.* **6 a** (1951) 32.
43. Preuner, G. and Schupp, W. *Z. physik. Chem.* **68** (1909) 129.
44. Klemm, W. and Kilian, H. *Z. physik. Chem.* **B49** (1941) 279.
45. Mooser, E. and Pearson, W. B. *Progress in Semiconductors* **5** (1960) 103.
46. Ruppel, W., Rose, A. and Gerritsen, H. *J. Helv. Phys. Acta* **30** (1957) 238.
47. Klemm, W. *Z. anorg. allgem. Chem.* **246** (1941) 347.
48. Angus, W. R. *Proc. Roy. Soc. (London)* **A 136** (1932) 573.

Received January 25, 1963.