On the Properties of Compounds with the ZrSe$_3$
Type Structure

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The compositions of the compounds TiS$_3$, ZrS$_3$, ZrSe$_3$, ZrTe$_3$, HfS$_3$, HfSe$_3$, and HfTe$_3$ are shown to be 1:3:0 by means of X-ray diffraction and density measurements. None of the compounds has an appreciable range of homogeneity. The ternary solid solution series ZrS$_3$–ZrSe$_3$–ZrTe$_3$ and HfS$_3$–HfSe$_3$–HfTe$_3$ have been investigated. ZrS$_{3-x}$Se$_x$ and HfS$_{3-x}$Se$_x$ exhibit continuous regions of solid solubility (0.00 \( \leq x \leq 3.00 \)); a limited solid solubility is found for ZrSe$_{3-x}$Te$_x$ and HfSe$_{3-x}$Te$_x$ (0.00 \( \leq x < \sim 0.1 \) and \( \sim 2.9 < x \leq 3.00 \)). Diffuse reflectance measurements show that ZrS$_{3-x}$Se$_x$ and HfS$_{3-x}$Se$_x$ exhibit semiconduction. No conclusions could be drawn as to the type of intrinsic electrical conduction of ZrTe$_3$ and HfTe$_3$ from their diffuse reflectance spectra. The binary compounds have diamagnetic susceptibilities.

The trichalcogenides \( (TX_3) \) of the Group IV A transition metals belong to an interesting class of isostructural compounds. Of the nine possible binary combinations of these elements, the existence of seven compounds with the ZrSe$_3$ type structure has been recorded in the literature, those lacking being the hitherto unreported compounds TiSe$_3$ and TiTe$_3$. Despite numerous studies\(^{1-17} \) only limited knowledge is at hand concerning the properties of these compounds. A complete crystal structure determination has, for example, so far only been carried out for the prototype ZrSe$_3$.\(^6,16 \) The compositions and homogeneity ranges of most of the compounds of this class have, furthermore, not been subjected to a systematic investigation. Except for the diamagnetic compounds TiS$_3$, ZrS$_3$, and HfS$_3$,\(^10 \) the magnetic properties of the compounds are not recorded in the literature. Even though the electrical and optical properties of the compounds have been the most widely studied,\(^7,10,14 \) a considerable amount of fundamental data are still lacking in this field. The object of the present paper is to report some new data on binary and ternary compounds with the ZrSe$_3$ type structure.
EXPERIMENTAL

The pure elements used in this study were turnings from crystal bars of 99.99 % Ti (A. D. Mackay, Inc.), 99.9 % Zr and 99.9 % Hf (Koch-Light Laboratories, Ltd.) and 99.9999 % S (Koch-Light Laboratories, Ltd.), 99.998 % Se (Bolidens Gruvaktiebolag, Sweden), and 99.999 % Te (Koch-Light Laboratories, Ltd.). (The analytical figure quoted for Hf excludes a content of ~3 % Zr.) Binary samples were prepared by heating weighed quantities of the components in sealed, evacuated silica tubes. Several samples with different initial compositions were made of each phase, on both sides of the stoichiometric 1:3 ratio. During the syntheses the temperature was slowly increased to 600(500)°C, the samples were kept at this temperature for 8−14 days, and then quenched in water. The samples were afterwards subjected to crushing and four further reannealings (with intermediate crushings) at 600(500)°C over a period of 30 days. The temperatures of the furnaces were kept constant to within ±1°C, using Getrosist (Philips) regulators in combination with a Philips reference chamber for the cold junctions of the Pt/Pt-Rh thermocouples. In order to minimize the effect of thermal gradients in the furnaces, the silica capsules were kept as short as possible and surrounded by quartz sand.

Single crystals of the binary phases were obtained by means of chemical transport reactions, using iodine as the transport agent in a concentration of ~5 mg/ml capsule volume. The specially constructed furnace and reaction vessels used for this purpose were made according to the recommendations of Schäfer.18 Further description of the transport conditions is presented in the results section.

In initial experiments, ternary samples were also made by heating weighed quantities of the components in sealed, evacuated silica tubes. However, despite a number of attempts to vary the experimental conditions, this method failed to give homogeneous samples. An alternative procedure was accordingly adopted, in which the binary compounds were mixed in proportions appropriate to the desired ternary compositions and heated at 600°C for 8 days. The samples were then crushed and reannealed at the same temperature, using 8 days intervals until X-ray powder photographs showed no further detectable changes in the composition equilibria.

X-Ray powder photographs of all samples were taken in a Guinier type camera of 80 mm diameter with monochromatized CuKα1-radiation (λ = 1.54050 Å) using KCl (α = 6.2919 Å19) as the internal standard. The lattice dimensions were refined by the method of least squares and the indicated error limits correspond to twice the standard deviations obtained in these calculations.

Density measurements were carried out pycnometrically at 25.00°C with kerosene as the displacement liquid. To remove gases adsorbed by the sample (weighing ~2 g), the pycnometer was filled with kerosene under vacuum.

Magnetic susceptibilities were measured between 80 and 1000 K by the Faraday method (maximum field ~8 kO) using 50−120 mg samples.

Diffuse reflectance measurements were made in the range 2 200−19 000 Å in a Cary 14 dual-beam spectrophotometer with diffuse reflectance accessory, using MgCO3 as a standard. The integrating sphere was coated with MgO, the samples being mounted in a specially constructed holder.

RESULTS AND DISCUSSION

(i) The binary compounds. Polycrystalline samples of TiS3, ZrS3, ZrSe2, ZrTe2, HfS3, HfSe3, and HfTe2 are easily synthesized by direct reactions between the elements. (Single phase samples of HfS3 and HfSe3 are most conveniently obtained with an initial atomic ratio X/T of > 3, the excess chalcogen being removed by cautious distillation after the reaction is completed.) Their existence is verified by the Guinier photographic data which moreover serve to confirm identities with the corresponding phases reported in the literature. Despite numerous attempts, it has hitherto proved impossible to prepare phases corresponding to the formulae TiSe3 and TiTe3.
COMPOUNDS WITH ZrSe₃ TYPE STRUCTURE

Table 1. Preparation temperatures, unit cell dimensions, and densities for compounds with ZrSe₃ type structure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Prep. temp. (°C)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>V (Å³)</th>
<th>dₓ-ray (g cm⁻³)</th>
<th>dpycn. (g cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiS₂</td>
<td>500</td>
<td>4.958(2)</td>
<td>3.4006(11)</td>
<td>8.778(4)</td>
<td>97.32(4)</td>
<td>146.8</td>
<td>3.259</td>
<td>3.233</td>
</tr>
<tr>
<td>ZrS₂</td>
<td>600</td>
<td>5.1243(11)</td>
<td>3.6244(10)</td>
<td>8.980(3)</td>
<td>97.28(2)</td>
<td>165.4</td>
<td>3.762</td>
<td>3.751</td>
</tr>
<tr>
<td>ZrSe₂</td>
<td>600</td>
<td>5.4109(12)</td>
<td>3.7488(9)</td>
<td>9.444(3)</td>
<td>97.48(2)</td>
<td>189.9</td>
<td>5.737</td>
<td>5.708</td>
</tr>
<tr>
<td>ZrTe₂</td>
<td>600</td>
<td>5.8939(14)</td>
<td>3.9259(12)</td>
<td>10.100(2)</td>
<td>97.82(2)</td>
<td>231.5</td>
<td>6.799</td>
<td>6.788</td>
</tr>
<tr>
<td>HfS₂</td>
<td>600</td>
<td>5.0923(11)</td>
<td>3.5052(7)</td>
<td>8.967(2)</td>
<td>97.38(2)</td>
<td>162.8</td>
<td>5.603</td>
<td>5.573</td>
</tr>
<tr>
<td>HfSe₂</td>
<td>600</td>
<td>5.388(2)</td>
<td>3.7216(10)</td>
<td>9.428(3)</td>
<td>97.78(3)</td>
<td>187.3</td>
<td>7.364</td>
<td>7.312</td>
</tr>
<tr>
<td>HfTe₂</td>
<td>500</td>
<td>5.879(2)</td>
<td>3.9022(9)</td>
<td>10.050(3)</td>
<td>97.98(3)</td>
<td>228.5</td>
<td>8.237</td>
<td>8.205</td>
</tr>
</tbody>
</table>

The unit cell dimensions of the phases at room temperature (Table 1), were found to be constant within experimental error for samples with different initial proportions. The implied lack of any appreciable ranges of homogeneity for these phases was confirmed by application of the disappearing phase principle to Guinier photograph of samples with different nominal compositions. When combined with visual inspection of the samples, the latter technique showed that the compounds obtain the stoichiometric 1:3 composition. The formula TX₃ was also confirmed by comparing the pycnometrically measured densities with those calculated from the unit cell dimensions on the assumption of two formula units per cell (Table 1).

A systematic search for suitable thermal conditions for the growth of large single crystals by chemical transport reactions was carried out as a part of the present work. The optimum conditions are summarized in Table 2 which shows that all the binary compounds are obtained by this technique. A successful preparation of HfTe₃ by this method depends rather critically on the choice of the temperatures t₁ and t₂ at the hot and cold zones of the reaction vessel, respectively (cf. Table 2 and Ref. 17). Although the transport conditions for HfSe₂ are less sensitive to the choice of t₁ and t₂ than for HfTe₂, t₁ must be ~700°C in order to facilitate reasonable crystal growth of the former compound. For ZrTe₃, on the other hand, t₁ and t₂ may be subjected

Table 2. Suitable thermal conditions for chemical transport reactions of TiS₂, ZrS₂, ZrSe₂, ZrTe₂, HfS₂, HfSe₂, and HfTe₂.

<table>
<thead>
<tr>
<th>Compound</th>
<th>t₁ (°C)</th>
<th>t₂ (°C)</th>
<th>Δt/l (°C/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiS₂</td>
<td>560</td>
<td>470</td>
<td>0.6</td>
</tr>
<tr>
<td>ZrS₂</td>
<td>800</td>
<td>620</td>
<td>1.2</td>
</tr>
<tr>
<td>ZrSe₂</td>
<td>800</td>
<td>630</td>
<td>1.1</td>
</tr>
<tr>
<td>ZrTe₂</td>
<td>850</td>
<td>630</td>
<td>1.5</td>
</tr>
<tr>
<td>HfS₂</td>
<td>800</td>
<td>580</td>
<td>1.5</td>
</tr>
<tr>
<td>HfSe₂</td>
<td>700</td>
<td>600</td>
<td>0.7</td>
</tr>
<tr>
<td>HfTe₂</td>
<td>520</td>
<td>470</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Acta Chem. Scand. 26 (1972) No. 9
to considerable variation, transport conditions being accomplished at $t_1 = 950^\circ C$, $t_2 = 800^\circ C$ as well as $t_1 = 800^\circ C$, $t_2 = 600^\circ C$. Large crystals were not obtained for HfS$_3$, which invariably gave an entangled network of small needle-shaped crystals as the product of transport reactions.

(ii) Ternary phases. During the investigation of the ternary solid solution series ZrS$_3$–ZrSe$_3$–ZrTe$_3$ and HfS$_3$–HfSe$_3$–HfTe$_3$ a considerable number of useless samples were made resulting from difficulties in obtaining true equilibria, and the results presented below correspond only to a small fraction of the samples prepared. Most of the preparative difficulties can be attributed to almost uncontrollable displacement reactions of the type

$$2\text{ZrSe}_3 + \text{ZrTe}_3 \rightarrow 3\text{ZrSe}_2 + 3\text{Te}$$

which take place parallel to the desired reactions (cf. Ref. 9).

The Guinier photographs of all samples which had achieved equilibria showed sharp reflections. Indexing was possible on the assumption that these samples contained one or two phases with monoclinic symmetry. The deduced unit cell dimensions (Figs. 1, 2) resemble those found for the corresponding binary compounds. The observed intensities of the reflections on

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**Fig. 1.** Unit cell dimensions of the ternary solid solution series ZrS$_3$–ZrSe$_3$–ZrTe$_3$ as functions of composition, where filled circles represent single-phase samples, and crosses represent two-phase samples. The estimated error limits do not exceed the size of the symbols.
the Guinier photographs confirm that the atomic arrangement is of the ZrSe$_3$ type, within the range of solid solution, the positional parameters having values close to those of the corresponding binary compounds. The lack of additional superstructure reflections on the Guinier photographs shows the substituted atoms to be arranged at random in the non-metal (X) sublattices.

For the phases ZrS$_{3-x}$Se$_x$ and HfS$_{3-x}$Se$_x$ there occur continuous regions of solid solubility, *i.e.* possible values of $x$ cover the entire range $0.00 \leq x \leq 3.00$. ZrSe$_3$ and ZrTe$_3$ as well as HfSe$_3$ and HfTe$_3$ show only slight mutual solubility, permitted values of $x$ being $0.00 \leq x < 0.1$ and $2.9 < x \leq 3.00$ in the formulae ZrS$_{3-x}$Te$_x$ and HfS$_{3-x}$Te$_x$.

As may be seen from Fig. 1, a substantially linear dependence on $x$ is found for $b$, $\beta$, and $V$ of the unit cell of the ZrS$_{3-x}$Se$_x$ phase, while the $a$ and $c$ axes show departures from linearity. A similar result is also obtained for the HfS$_{3-x}$Se$_x$ phase (Fig. 2).

Hume-Rothery's 20 necessary, but insufficient condition, governing the possible substitution of one kind of atom for another in a crystalline phase, requires that the radii of the atoms concerned should be within about 15% of each other. This requirement is satisfied for the combination sulphide-selenide ($r_{Se}/r_S = 1.12$), whereas the combination selenide-telluride ($r_{Te}/r_{Se} = 1.16$) belongs to the borderline cases. The present results (*vide supra*) are accordingly consistent with Hume-Rothery's rule. The degree of mutual solubility is, on the other hand, also partially controlled by the compatibility or otherwise of the electronic band structures for the solvent and solute phases.21,22 On this basis it is tempting to suggest that there is a significant difference between the electronic band structures of ZrS$_3$ and ZrSe$_3$ (HfS$_3$ and HfSe$_3$) on the one hand and ZrTe$_3$ (HfTe$_3$) on the other. The compatibility of these electronic band structures is to some extent evinced by the electrical conduc-

tion properties of the compounds. In line with this view, ZrS₃, ZrSe₃, HfS₃, and HfSe₃ are all semiconducting, whereas ZrTe₃ and HfTe₃ either are metallic type of conductors or semiconductors with very small band gaps ($\Delta E \leq 0.2$ eV, see section iii).

Figs. 1 and 2 show deviations from Vegard's law²³,²⁴ in respect of the axes a and c, the departures having a similar character for a given axis of the ZrSₓ₋₃⁻ₓSeₓ and HfSₓ₋₃⁻ₓSeₓ phases. The origin of these findings is probably associated with the systematic variations in the eight positional parameters of the ZrSe₃ type structure which are likely to occur as functions of composition within the homogeneity ranges.

(iii) Diffuse reflectance. The diffuse reflectance spectra of ZrSₓ₋₃⁻ₓSeₓ for different x, shown in Fig. 3, may be taken as representative also of the spectra obtained for TiSₓ and HfSₓ₋₃⁻ₓSeₓ. The spectra of ZrTe₃ and HfTe₃ show a slight, but uniform increase in log $R_0/R$ between 2 000 and 19 000 Å, with no observed absorption edge or other characteristic features. Repeated measurements on different samples show that the results are well reproducible.

The evaluation of the band gap ($\Delta E$) from diffuse reflectance spectra depends on the determination of the location of the absorption edge. Using the extrapolation method recommended by Tandon and Gupta²⁵ values of 0.83 ± 0.04, 1.91 ± 0.06, 1.11 ± 0.04, 1.95 ± 0.06, and 1.02 ± 0.04 eV are obtained.

![Diffuse reflectance spectra](image)

Fig. 3. Diffuse reflectance spectra of various samples of the ZrSₓ₋₃⁻ₓSeₓ phase.

for $\Delta E$ of TiS$_3$, ZrS$_3$, ZrSe$_3$, HfS$_3$, and HfSe$_3$, respectively. Except for HfSe$_3$, the values are reasonably consistent with those reported by Grimmeiss et al.$^{14}$ Fig. 4 shows that $\Delta E$ decreases approximately linearly with $x$ for the ZrS$_{3-x}$Se$_x$

\[ \text{Fig. 4. Band gap ($\Delta E$) versus $x$ in ZrS$_{3-x}$Se$_x$.} \]

phase. This finding appears to justify a linear extrapolation of the $\Delta E$-values for ZrS$_3$ and ZrSe$_3$, and HfS$_3$ and HfSe$_3$ to ZrTe$_3$ and HfTe$_3$, respectively, giving $\Delta E \approx 0.2$ eV in both cases. The fact that the generalized $(8-N)$ rule is satisfied for the compounds with ZrSe$_3$ type structure (see section v) may be taken as an indication of ZrTe$_3$ and HfTe$_3$ being semiconductors with small band gaps rather than metallic type of conductors (cf. Ref. 10).

(iv) Magnetic susceptibility. The results of the magnetic susceptibility measurements are presented in Table 3. By the introduction of slight approximations in some cases, it proved possible to express the $\chi$ versus $T$ relationships in analytical form for all compounds. The data are uncorrected for induced diamagnetism since reliable corrections are not easily estimated. All the compounds are diamagnetic with essentially temperature independent susceptibilities, the results for TiS$_3$, ZrS$_3$, and HfS$_3$ being in excellent agreement with those reported earlier.$^{18}$

(v) Chemical bonding. The ZrSe$_3$ type crystal structure comprises three non-equivalent $X$ atoms according to the crystallographic formula $TX_1X_{11}X_{111}$.

Table 3. Magnetic susceptibility data for binary compounds with the ZrSe$_3$ type structure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\chi_s \times 10^4$ in e.m.u./g;</th>
<th>temperature range in K</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiS$_3$</td>
<td>$-0.09 \pm 0.01$;</td>
<td>80 - 700</td>
</tr>
<tr>
<td>ZrS$_3$</td>
<td>$-0.19 \pm 0.01$;</td>
<td>80 - 700</td>
</tr>
<tr>
<td>ZrSe$_3$</td>
<td>$-0.33 \pm 0.02$;</td>
<td>80 - 850</td>
</tr>
<tr>
<td>ZrTe$_3$</td>
<td>$-0.41 \pm 0.000018T$;</td>
<td>80 - 1000</td>
</tr>
<tr>
<td>HfS$_3$</td>
<td>$-0.21 \pm 0.01$;</td>
<td>80 - 700</td>
</tr>
<tr>
<td>HfSe$_3$</td>
<td>$-0.40 \pm 0.02$;</td>
<td>80 - 850</td>
</tr>
<tr>
<td>HfTe$_3$</td>
<td>$-0.46 \pm 0.02$;</td>
<td>80 - 750</td>
</tr>
</tbody>
</table>

The coordination around the $T$, $X_I$, $X_{II}$, and $X_{III}$ atoms can be seen from Fig. 5. Each $T$ atom is surrounded by six near $X$ (two $X_I$, two $X_{II}$, and two $X_{III}$) atoms at the corners of a triangular prism and by two near $X_I$ atoms outside two of the rectangular faces of the prism. The $X_I$ atoms are coordinated to four near $T$ atoms arranged at the corners of a deformed tetrahedron. The $X_{II}(X_{III})$ atoms are coordinated to two near $T$ atoms and one near $X_{III} (X_{II})$ atom. The coordination polyhedra of $X_{II}$ and $X_{III}$ can be regarded as distorted tetrahedra with one corner vacant. The arrangement of the $X_{II}$ and $X_{III}$ atoms produces $X_{II}-X_{III}$ pairs with short interatomic distances. The short distance within the $Se_{II}-Se_{III}$ pairs of the ZrSe$_3$ structure (2.34 Å$^{16}$) is in reasonable agreement with the corresponding expectation value for a single Se-Se bond.

With this information it is now possible to test these compounds in terms of the generalized (8−N) rule (cf., e.g., Ref. 26). Assuming that each $X$ atom obtains a complete octet in its valence shell (implying that each $X_{II}$ and $X_{III}$ atom must carry a lone electron pair), the correct mathematical formulation of the rule is in this case $n + P - Q = 8-a$, where, per formula unit, $n$ is the total number of electrons involved in bonding, $P$ and $Q$ are the number of electrons in $X-X$ and $T-T$ bonds, respectively, and $a$ is the number of $X$ atoms. In accordance with previous experience and the observed diamagnetism for the compounds, each $T$ atom is assumed to contribute 4 electrons and each $X$ atom 6 electrons to $n(=22)$, i.e. the valence states of the constituent atoms correspond to their group number of the Periodic Table. The structural data unequivocally show that $P = 2$ and $Q = 0$ and the composition $TX_3$ gives $a = 3$. The values $n = 22$, $P = 2$, $Q = 0$, and $a = 3$ satisfy...
the above equation and the observed semiconductivity for TiS₃, ZrS₃, ZrSe₃, HfS₃, and HfSe₃ provides complete tests of the validity of the generalized (8−N) rule.

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