On the Crystal Structures of ZrSb$_2$ and α-HfSb$_2$

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The compositions of the compounds TiAs$_2$, ZrSb$_2$, and α-HfSb$_2$ are shown to be 1:2.00 by means of X-ray diffraction and density measurements. None of the compounds has an appreciable range of homogeneity. The TiAs$_2$ type crystal structure of ZrSb$_2$ and α-HfSb$_2$ has been ascertained on the basis of three-dimensional, single crystal X-ray data.

The "theoretical" treatment of chemical bonding in chalcogenides and pnictides of the transition metals (T) is characterized by a demarcation at some $50-60$ atomic % of the non-metal component (X). A metallic type of bonding is usually found in compounds on the metal-rich side of this composition. This kind of bonding is not well understood because of the need to take account of the complex band structure description of delocalized electron configurations. For compounds of the form T_2X_3 and higher non-metal content, on the other hand, a covalent description has often been used with success, as exemplified by the applicability of the generalized $(8-N)$ rule.[1-5]

Within the latter class of compounds, those including metals from Groups IVA to VIA are in many cases poorly understood compared with those from Groups VIIA and VIIIA. This is partly due to a lack of data. In varying the metal component from those of Group IVA to VIIIA the coordination around T changes from mainly trigonal prismatic, cubic anti-prismatic, or variants, to octahedral, the transition occurring fairly sharply between the Groups VIA and VIIA. Similar considerations apply to the coordinations of the non-metal atoms.

A programme of research on compounds with $X > 60$ atomic % and with T from the Groups IVA – VIA is in progress at this Institute. The compounds chosen for an investigation of composition and crystal structure are TiAs$_2$, ZrSb$_2$, and α-HfSb$_2$, which have been reported earlier.[6-8]

EXPERIMENTAL

The pure elements used in this study were 99.999 % Ti, 99.9 % Zr, 99.9 % Hf (A. D. MacKay or Koch-Light Laboratories; turnings from crystal bars), 99.999 + % As (Fluka), and 99.999 + % Sb (Johnson, Matthey & Co.).

Polycrystalline samples for the phase analyses were prepared by heating weighed quantities of the components in evacuated and sealed silica tubes at 800°C for 15 days. After careful grinding, the samples were reannealed at 800°C for another 15 days and finally quenched in ice-water or cooled to room temperature over a period of 5 days. The temperature of the furnaces was kept constant to within ± 0.5°C, using Getrosist (Philips) regulators in combination with a Frigistor 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. Several samples with different initial compositions were made of each phase, on both sides of the stoichiometric 1:2 ratio.

Single crystals of $ZrSb_2$ and α-$HfSb_2$ were formed by chemical transport reactions, using iodine (~ 1 mg/ml capsule volume) as transport agent. A temperature gradient of ~ 1°C/mm was applied along ~ 200 mm long (evacuated and sealed) silica capsules, while their hot ends, containing the polycrystalline $ZrSb_2$ and α-$HfSb_2$ samples, were heated at ~ 800°C. These conditions produced a considerable number of crystals at the cold ends of the capsules after 7 days.

X-Ray photographs of crushed crystals were taken in a Guinier type focusing camera of 80 mm diameter with monochromatized $CuK\alpha_1$-radiation ($\lambda = 1.54050$ Å) using KCl ($\lambda = 6.2919$ Å) as internal standard.

Three-dimensional single crystal data were collected with an integrating Weissenberg camera of 57.3 mm diameter with Zr-filtered $MoK\alpha$-radiation using the multiple-film technique. The intensities were measured microphotometrically except for the weakest reflections which were estimated visually by comparison with a standard scale. The intensities were corrected for the combined Lorentz and polarization factors, and for absorption (the crystal shapes being approximately cylindrical) and secondary extinction.

The calculations, including least squares refinements of the unit cell dimensions, corrections, data reduction, scalings, and full matrix least squares refinements of the structure factors, and calculations of interatomic distances and angles, were performed on the electronic computers UNIVAC 1107 and CD 3300 using in most cases programmes by Dahl et al.[10]

The atomic scattering factors used in the calculations of F_c-values were taken from Hanson et al.[11] The extent of the agreement between the observed and calculated structure factor data is judged from the reliability factor $R = \sum ||F_o| - |F_c||/\sum |F_o|$. The unobserved reflections are not included in the calculations of R, and are omitted from the least squares refinements. Throughout this paper the calculated standard deviations are appended in brackets after the corresponding parameter values, only the last digit(s) being given in each case.

The density measurements were made pycnometrically at 25.00°C with kerosene as displacement liquid. To remove gases adsorbed by the samples (weighing ~ 2 g) the pycnometer was filled with kerosene under vacuum.

RESULTS AND DISCUSSION

(i) *Homogeneity range, composition, and unit cell dimensions.* The existence of the $TiAs_2$, $ZrSb_2$, and α-$HfSb_2$ phases is verified by the X-ray diffraction data, which moreover serve to confirm identities with the corresponding phases reported in the literature.[6-8] The unit cell dimensions of the phases, as determined from Guinier photographs taken at room temperature, 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 photographs of samples with different nominal compositions. When combined with visual inspection of the samples, the latter technique showed the compounds to be stoichiometric within the limits defined by the formula $TX_{2.00 \pm 0.03}$. The stoichiometric 1:2 compositions were also confirmed by

Table 1. Structural data for $TiAs_2$, $ZrSb_2$, and α-$HfSb_2$. The positional parameters and temperature factors for $TiAs_2$ are quoted from Wenglowski *et al.*[7]

Compound	a (Å)	b (Å)	c (Å)	Atomic parameters			
				Atom	x	y	B (Å²)
$TiAs_2$	13.2303(10)	8.9147(7)	3.4793(4)	Ti_I	0.245	0.517	0.2
				Ti_{II}	0.007	0.331	0.2
				As_I	0.440	0.613	0.2
				As_{II}	0.163	0.836	0.2
				As_{III}	0.200	0.225	0.2
				As_{IV}	0.400	0.011	0.2
$ZrSb_2$	14.9684(8)	9.9672(6)	3.8813(3)	Zr_I	0.2509(11)	0.5231(19)	0.28(4)
				Zr_{II}	0.0067(11)	0.3277(20)	0.26(4)
				Sb_I	0.4414 (9)	0.6145(13)	0.32(5)
				Sb_{II}	0.1569 (9)	0.8393(14)	0.33(5)
				Sb_{III}	0.1986 (8)	0.2320(13)	0.33(4)
				Sb_{IV}	0.3978 (9)	0.0105(13)	0.33(5)
α-$HfSb_2$	14.9890(9)	9.8781(5)	3.8506(3)	Hf_I	0.2492 (8)	0.5281(15)	0.41(5)
				Hf_{II}	0.0076 (8)	0.3299(13)	0.43(4)
				Sb_I	0.4416 (6)	0.6146(10)	0.35(4)
				Sb_{II}	0.1578 (6)	0.8395(10)	0.36(5)
				Sb_{III}	0.1989 (5)	0.2353 (9)	0.34(4)
				Sb_{IV}	0.3968 (6)	0.0127 (9)	0.34(4)

comparing the pycnometrically measured densities (6.36, 7.63, and 9.80 g cm⁻³ for $TiAs_2$, $ZrSb_2$, and α-$HfSb_2$, respectively) with those calculated from the unit cell dimensions on the assumption of 8 TX_2-groups per cell.

The lattice dimensions (with associated standard deviations) listed in Table 1 have been obtained as average values for several independently synthesized samples.

(ii) *Refinement of the structures.* The systematic extinctions in the diffraction data are of the type $0kl$ absent when $k+l=2n+1$ and $h0l$ absent when $h+l=2n+1$, implying that the possible space groups are limited to $Pnnm$ and $Pnn2$. The highest symmetric space group $Pnnm$ was chosen by Wenglowski *et al.*[7] to describe the structure of the prototype $TiAs_2$, which, however, neglects the fact that essentially the same atomic arrangement is also generated by $Pnn2$. The latter space group lacks the mirror planes of symmetry perpendicular to [001] at $z=0$ and $z=\frac{1}{2}$, which are characteristic of the former. The problem is thus completely analogous to that encountered for the FeS_2-m (m = marcasite) type structure.[12,13] However, the situation with respect to the $TiAs_2$ type structure is considerably more complicated due to the fact that the number of variable parameters required to specify the latter type structure is of the order of six times greater than for the FeS_2-m type, depending on the models used in the comparison. With this in view, and being furthermore aware of the fact that the quantity and quality of the intensity data for $ZrSb_2$ and α-$HfSb_2$ do not permit of proper statistical testing in order to resolve this ambiguity (*cf.*, *e.g.*, Refs. 12 and 13), the highest symmetric space group is also postulated in the present investigation.
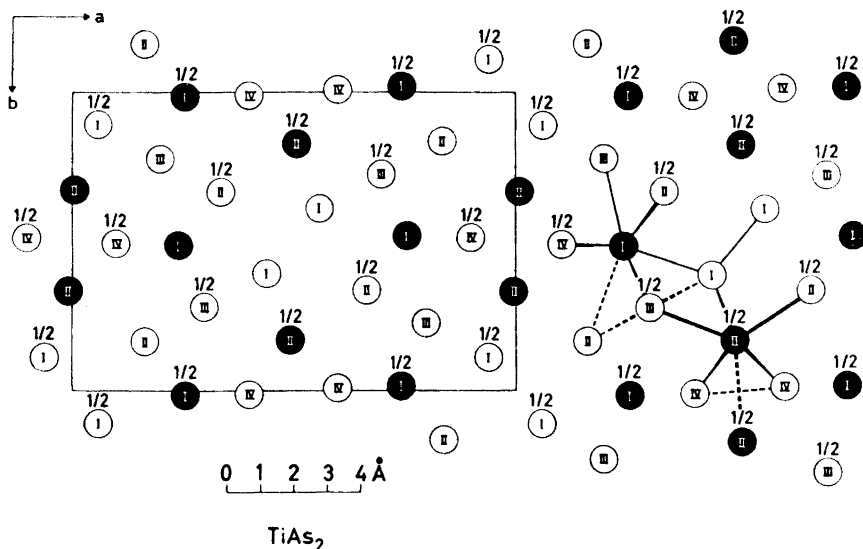
Fig. 1. The $TiAs_2$ type crystal structure projected along [001]. Filled and open circles represent metal (T) and non-metal (X) atoms, respectively. Heavy solid lines denote bonding interatomic distances, broken lines indicate possible bonding interatomic distances.

In terms of space group *Pnnm* the $TiAs_2$ type structure (Fig. 1) places $4T_I$, $4T_{II}$, $4X_I$, $4X_{II}$, $4X_{III}$, and $4X_{IV}$ atoms in position $4(g)$: $\pm (x,y,0;\frac{1}{2}+x, \frac{1}{2}-y,\frac{1}{2})$. Twelve positional parameters are accordingly necessary in order to specify the location of all atoms within the unit cell (*cf.* Table 1) and the assumption of isotropic thermal motion of all atoms adds six further parameters. (The allowance for anisotropic temperature factors in the first refinement cycles led to standard deviations in these parameters, which exceeded the deviations from isotropy. This possibility was consequently excluded in the final calculations.)

The assignment of $TiAs_2$ type structure to $ZrSb_2$ and α-$HfSb_2$ was immediately verified and least squares refinements were begun at once. There was no problem associated with these calculations which were continued until no shifts were produced in any variable. The final parameters, including isotropic temperature factors with standard deviations, are given in Table 1, the corresponding R-values being 0.113 and 0.098 for $ZrSb_2$ and α-$HfSb_2$, respectively.

(iii) *Interatomic distances and angles.* The atomic arrangement of the $TiAs_2$ type structure is shown in Fig. 1 and some important interatomic distances and angles calculated from the structural data in Table 1 are listed in Table 2.

The T_I and T_{II} atoms have essentially the same configuration of eight near X neighbours. Six of these X atoms are at the corners of a right triangular prism and two lie outside the rectangular faces of the prism. The triangular prismatic arrangement comprises two X_{II}, two X_{III}, and two X_{IV} atoms in

Table 2. Interatomic distances and angles in the crystal structures of TiAs$_2$, ZrSb$_2$, and α-HfSb$_2$.

Interatomic distances (Å)

Type		TiAs$_2$	ZrSb$_2$	α-HfSb$_2$
Bonding interatomic distances	$T_I - X_I$ (1)	2.72	2.993(21)	3.008(15)
	$T_I - X_{II}$ (2)	2.67	3.004(17)	3.020(13)
	$T_I - X_{III}$ (2)	2.64	2.945(17)	2.916(13)
	$T_I - X_{III}$ (1)	2.67	3.005(23)	2.989(17)
	$T_I - X_{IV}$ (2)	2.59	2.956(15)	2.919(11)
	$T_{II} - X_I$ (2)	2.70	2.981(18)	2.968(12)
	$T_{II} - X_{II}$ (1)	2.70	2.961(22)	2.991(15)
	$T_{II} - X_{III}$ (1)	2.72	3.027(21)	3.016(14)
	$T_{II} - X_{IV}$ (2)	2.65	3.004(17)	2.980(11)
	$T_{II} - X_{IV}$ (2)	2.67	3.021(17)	3.003(12)
	$X_I - X_I$ (1)	2.56	2.879(18)	2.862(14)
Possible bonding interatomic distances	$T_I - X_{II}$ (1)	3.04	3.451(23)	3.367(17)
	$X_I - X_{III}$ (2)	2.73	3.087(15)	3.092 (9)
	$X_{II} - X_{III}$ (2)	2.70	3.096(15)	3.063 (9)
	$X_{IV} - X_{IV}$ (1)	2.65	3.067(17)	3.104(13)
	$T_{II} - T_{II}$ (1)	3.02	3.441(28)	3.368(18)
Shortest interatomic distances neglected as bonding	$T_I - X_I$	4.32	4.806(21)	4.844(15)
	$X_{III} - X_{IV}$	3.26	3.682(15)	3.643(11)
	$T_{I(II)} - T_{I(II)}$	3.4793(4)	3.8813(3)	3.8506(3)

Interatomic angles (°)

Type	TiAs$_2$	ZrSb$_2$	α-HfSb$_2$	Type	TiAs$_2$	ZrSb$_2$	α-HfSb$_2$
$X_I - T_I - X_{III}$ (1)	121.2	121.1(5)	121.1(5)	$T_{II} - X_I - T_{II}$ (1)	80.2	81.2(5)	80.9(3)
$X_{II} - T_I - X_{II}$ (1)	81.4	80.5(5)	79.2(4)	$X_I - X_I - T_I$ (1)	109.9	109.8(6)	111.2(5)
$X_{II} - T_I - X_{III}$ (2)	82.5	83.5(4)	83.6(3)	$X_I - X_I - T_{II}$ (2)	113.9	114.0(5)	114.2(4)
$X_{III} - T_I - X_{IV}$ (2)	83.5	84.0(4)	83.9(3)	$T_I - X_{II} - T_I$ (1)	81.4	80.5(5)	79.2(3)
$X_{III} - T_I - X_{III}$ (1)	82.2	82.4(5)	82.7(4)	$T_I - X_{II} - T_{II}$ (2)	135.6	136.3(4)	136.7(2)
$X_{III} - T_I - X_{IV}$ (2)	77.1	77.9(4)	78.5(3)	$T_I - X_{III} - T_I$ (1)	82.2	82.4(5)	82.7(3)
$X_{IV} - T_I - X_{IV}$ (1)	84.4	82.1(5)	82.5(4)	$T_I - X_{III} - T_I$ (2)	128.5	128.0(5)	127.7(3)
$X_I - T_{II} - X_I$ (1)	80.2	81.2(5)	80.9(4)	$T_I - X_{III} - T_{II}$ (1)	82.5	86.7(6)	86.6(4)
$X_I - T_{II} - X_{IV}$ (2)	83.9	83.6(4)	83.8(3)	$T_I - X_{III} - T_{II}$ (2)	120.1	117.8(5)	118.1(3)
$X_I - T_{II} - X_{IV}$ (2)	95.7	95.9(3)	95.6(2)	$T_I - X_{IV} - T_I$ (1)	84.4	82.1(4)	82.5(3)
$X_{II} - T_{II} - X_{III}$ (1)	126.2	127.4(8)	127.9(5)	$T_I - X_{IV} - T_{II}$ (2)	85.2	87.7(4)	88.1(3)
$X_{IV} - T_{II} - X_{IV}$ (2)	59.9	61.2(4)	62.5(3)	$T_I - X_{IV} - T_{II}$ (2)	86.8	87.8(4)	88.0(3)
$X_{IV} - T_{II} - X_{IV}$ (1)	81.4	79.9(5)	79.7(3)	$T_{II} - X_{IV} - T_{II}$ (2)	69.2	69.6(5)	68.5(3)
$X_{IV} - T_{II} - X_{IV}$ (1)	82.1	80.5(5)	80.5(3)	$T_{II} - X_{IV} - T_{II}$ (1)	81.4	79.9(4)	79.7(3)
$T_I - X_I - T_{II}$ (2)	118.2	117.7(5)	116.7(4)	$T_{II} - X_{IV} - T_{II}$ (1)	82.1	80.5(4)	80.5(3)

the case of the T_I atoms and two X_I and four X_{IV} atoms surround the T_{II} atoms in a similar manner. One X_I and one X_{III} atoms complete the coordination polyhedron around the T_I atoms, their counterparts being one X_{II} and one X_{III} atoms in the case of the T_{II} atoms. Each T_I atom has also one X_{II} atom as an additional, fairly close neighbour, but the corresponding interatomic distance is significantly longer than the other short interatomic $T-X$ distances (cf. Table 2). Similarly, it may be possible to argue that an additional T_{II} atom belongs to the coordination polyhedron of the T_{II} atoms.

The four crystallographically non-equivalent X atoms of the $TiAs_2$ type structure exhibit different immediate surroundings. Each X_I atom is coordinated to three near T (one T_I and two T_{II}) atoms and one near X_I atom in a distorted tetrahedral configuration. The coordination polyhedron of the two near T_I and one near T_{II} atoms around the X_{II} atoms can be considered as a distorted tetrahedron with one of the corners vacant. The X_{III} atoms have three T_I and one T_{II} atoms as near neighbours in a distorted tetrahedral arrangement. Each X_{IV} atom is in a trigonal prismatic coordination of two near T_I and four near T_{II} atoms. In addition, each X_I atom has two X_{III} atoms, each X_{II} atom has one T_I and two X_{III} atoms, each X_{III} atom has two X_I and two X_{II} atoms, and each X_{IV} atom has one X_{IV} atom as fairly close neighbours (cf. Table 2 and Fig. 1).

As shown in Table 2, it is convenient to consider three categories of interatomic distances in the $TiAs_2$ type structure. The lengths of the shortest $T-X$ $(,X-T,)$ and $X-X$ distances listed in the table are consistent with these being bonding distances. The shortest X_I-X_I distance in $ZrSb_2$ and α-$HfSb_2$ is in good agreement with the expectation value for the single bond $Sb-Sb$ distance suggested by Furuseth et al.[14], whereas the corresponding distance in $TiAs_2$ is somewhat longer than the expected single bond $As-As$ distance.

In addition to the clearly defined bonding $T-X$ and $X-X$ distances, there also occur some relatively short $T-X$, $X-X$, and $T-T$ distances which cannot definitely be regarded as non-bonding distances. In fact, all distances belonging to this category appear to be too great to represent normal single bonds, but also seem too short for there to be negligible bonding interaction. Further experiments are undoubtedly necessary to determine the character of these possible bonding distances. However, this ambiguity, together with the unusual coordination of the X_{IV} atoms (in relation to other TX_2 compounds); the generally low symmetry of the coordination polyhedra; and the wide range of bonding $T-X$ distances; suggest that the bonding scheme for the compounds with the $TiAs_2$ type structure is rather complicated. It is not surprising, therefore, to find that endeavours to arrive at a bonding scheme based on the generalized $(8-N)$ rule [1-5] have been in vain. Consistent with this, $TiAs_2$, $ZrSb_2$, and α-$HfSb_2$ have been reported [8] to exhibit a metallic type of conduction.

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