

The Crystal Structure of HfTe_5

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The crystal structure of HfTe_5 has been determined from three dimensional X-ray data. The structure is orthorhombic, space group *Cmcm*. The pycnometric density at 25.00°C is 6.806 gcm^{-3} , the unit cell contains four formula units, and has the dimensions: $a = 3.9743(5) \text{ \AA}$, $b = 14.492(2) \text{ \AA}$, $c = 13.730(2) \text{ \AA}$. The following values were found for the positional parameters: $y = 0.3143(1)$ for Hf in 4(c); $y = 0.6635(2)$ for Te_I in 4(e); $y = 0.9299(2)$, $z = 0.1494(2)$ for Te_{II} in 8(f); $y = 0.2099(2)$, $z = 0.4353(2)$ for Te_{III} in 8(f).

ZrTe_5 is shown to be isostructural with HfTe_5 ($d_{\text{pycn.}} = 6.079 \text{ gcm}^{-3}$; $a = 3.9876(11) \text{ \AA}$, $b = 14.502(4) \text{ \AA}$, $c = 13.727(3) \text{ \AA}$); both compounds are diamagnetic.

The HfTe_5 type structure comprises distinct layers arranged approximately parallel to (010). Within the layers distorted bi-capped trigonal prisms are linked together by zig-zag chains of Te atoms. The structure and bonding in HfTe_5 are discussed in relation to the ZrSe_5 type structure.

Some few years ago the development of inorganic chemistry had approached a stage when it was considered profitable to discuss the non-existence of particular compounds. However, the probable discovery of further compounds as a result of the *systematic* application of conventional and modern techniques of synthesis renders such an approach ill advised at the present time. Among the new compounds which continue to be discovered, some unexpected and strange compositions emerge at intervals. The recent preparation¹ of HfTe_5 has provided an interesting addition to the latter category. At first sight, the tellurium content of this compound seemed revolutionary high, but after a little while one gets accustomed to its existence and one aspires to place HfTe_5 in an ulterior chemical connection. The present report on the determination of its crystal structure represents a first step in this direction.

EXPERIMENTAL

Samples were prepared from 99.9 % Zr and Hf (turnings from crystal bars; the analytical figure for Hf excludes a content of ~3 % Zr) and 99.999 % Te from Koch-Light Laboratories, Ltd. Polycrystalline samples of ZrTe_5 and HfTe_5 were obtained by heating weighed quantities of the components in sealed, evacuated silica tubes at 450°C for 7 d

and cooling to room temperature over a period of 3 d. In preliminary¹ experiments, the use of too high temperature, $\geq 500^\circ\text{C}$, prevented the preparation of HfTe_5 by direct reaction.

Single crystals of both compounds were obtained by means of chemical transport reactions, using iodine as the transport agent in a concentration of 5 mg/ml capsule volume. The most suitable transport conditions were obtained by applying temperature gradients of ~ 1 ($\sim \frac{1}{3}$) $^\circ\text{C}/\text{mm}$ along ~ 150 mm long evacuated and sealed silica capsules, with the hot ends containing mixtures of Zr and Te (Hf and Te) at ~ 580 (~ 500) $^\circ\text{C}$. These conditions produced a considerable number of needle shaped crystals at the cold ends of the capsules after 7 days.

In analogy with ZrTe_5 and HfTe_5 attempts have also been made to prepare TiTe_5 . A variety of different thermal and transport conditions were tried during these syntheses, but this endeavour has hitherto failed.

X-Ray powder photographs of all samples were taken in a Guinier type camera of 80 mm diameter with monochromatized $\text{CuK}\alpha_1$ -radiation using KCl as internal standard.

Three dimensional single crystal data for HfTe_5 were collected (from the layers $0kl$ to $5kl$) in an integrating Weissenberg camera of 57.3 mm with Zr-filtered $\text{MoK}\alpha$ -radiation, using the multiple-film technique. The intensities were measured microphotometrically except for the weakest reflections, which were estimated visually. The intensities were corrected for the combined Lorentz and polarization factors, and for absorption according to the actual shape of the crystal. (No corrections for dispersion and secondary extinctions were carried out.)

The computational work, including least squares refinements of the unit cell dimensions, corrections, data reductions, scalings, Patterson- and Fourier-syntheses, full matrix least squares refinements of the structure factors, and calculations of interatomic distances and angles, was carried out on a CDC 3300 computer using, in most cases, the programmes of Dahl *et al.*²

Atomic scattering factors were taken from Hanson *et al.*³ Anisotropic thermal motion of the atoms were allowed for according to the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. The extent of the agreement between the observed and calculated structure factor data is judged from the average and weighted reliability factors $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ and $R^* = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]}{2}$ where w denotes the weight factor. The unobserved reflections were not included in the calculations of R and R^* , and were omitted from the least squares refinements. (The observed and calculated structure factor data are available from the authors upon request.)

Density measurements were carried out 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.

Magnetic susceptibilities were measured between 80 and 725 K by the Faraday method (maximum field ~ 8 kO) using 50–100 mg samples.

Diffuse reflectance measurements were made in the range 2200 to 22 000 \AA using a Cary 14 dual-beam spectrophotometer fitted with a diffuse reflectance accessory. MgCO_3 was used as a standard, and the integrating sphere was coated with MgO.

CRYSTAL DATA

ZrTe_5 , $M = 729.22$; HfTe_5 , $M = 816.49$.

Needle shaped single crystals with approximately rectangular cross section, a -axis along the needle axis.

Orthorhombic.

ZrTe_5 : $a = 3.9876(11)$ \AA , $b = 14.502(4)$ \AA , $c = 13.727(3)$ \AA ,
 $V = 793.8(6)$ \AA^3

HfTe_5 : $a = 3.9743(5)$ \AA , $b = 14.492(2)$ \AA , $c = 13.730(2)$ \AA ,
 $V = 790.8(3)$ \AA^3

Observed densities at 25.00°C.

ZrTe₅: 6.079 gcm⁻³

HfTe₅: 6.806 gcm⁻³

Unit cell content: 4 TX_5 groups.

Systematic extinctions:

hkl absent when $h+k=2n+1$

$h0l$ absent when $l=2n+1$ (and/or $h=2n+1$)

Space group: $Cmcm$ (the possible space groups $C2cm$ and $Cmc2_1$ were excluded as a result of the structure determination).

STRUCTURE DETERMINATION OF HfTe₅

With great zest the structure determination of HfTe₅ was started before no more than the intensity data from the layer $0kl$ had been evaluated. The (100) Patterson projection contains a large number of poorly resolved peaks. However, the composition HfTe₅ in relation to the space group symmetry and the short a -axis greatly aids the interpretation of the Patterson map. Furthermore, on taking advantage of postulated similarities with key fragments of the crystal structures of ZrSe₃^{4,5} and elemental Te^{6,7} and the expected values for the Hf-Te and Te-Te bond lengths it was in fact a relatively simple task to devise a useful trial structure. The tentative atomic positions were improved by application of the minimum residual method, by Fourier syntheses, and finally by least squares refinements until termination at $R=0.083$.

The three dimensional atomic arrangement of HfTe₅ is approximately fixed on the basis of the coordinates in the (100) projection. There is, in fact, only a slight degree of freedom for the variations of the x parameters from the fixed values of 0 and $\frac{1}{2}$ prescribed by space group $Cmcm$. (Space group $Cmc2_1$ was eliminated from the (100) projection and at this stage there was accordingly a choice between $Cmcm$ and $C2cm$.)

Refinements of the three dimensional structure factor data, according to the method of least squares, were carried out assuming a description of the

Table 1. Final positional and thermal parameters for the crystal structure of HfTe₅.

(Hf and Te_I in position 4(c) and Te_{II} and Te_{III} in position 8(f) of space group $Cmcm$. The symmetry of $Cmcm$ imposes the restraint $\beta_{12}=\beta_{13}=0$ on all atoms and in addition $\beta_{23}=0$ on Hf and Te_I. According to the calculations β_{23} is zero for Te_{II} and Te_{III}, thus confining the principal axes of the vibrational ellipsoids to coincide with the crystallographic axes for all atoms.)

	Hf	Te _I	Te _{II}	Te _{III}
y	0.3143(1)	0.6635(2)	0.9299(2)	0.2099(2)
z	$\frac{1}{4}$	$\frac{1}{4}$	0.1494(2)	0.4353(2)
β_{11}	0.0121(12)	0.0064(17)	0.0109(13)	0.0134(13)
β_{22}	0.0010(1)	0.0010(1)	0.0017(1)	0.0013(1)
β_{33}	0.0010(1)	0.0011(1)	0.0017(1)	0.0012(1)

structure in terms of space group $C2cm$. The least squares iterations were continued until no shifts were obtained in any of the variables for each computational model. Using the Hamilton⁸ test it was found that the model specified by the positional and thermal parameters listed in Table 1 ($R=0.053$ and $R^*=0.034$ for 484 independent reflections), is superior to all models based on variable x parameters at a significance level <0.005 . The conclusion reached by application of the Hamilton test concurs with that derived from the values of the parameters for the various models and their associated standard deviations, *viz.* that space group $Cmcm$ gives the most correct description of the crystal structure of $HfTe_5$. The correctness of the structure was finally also ascertained by a difference Fourier synthesis.

Obvious relationships in dimensions, content, and symmetry of the unit cells (*vide supra*) and nearly matching intensities on Guinier and Weissenberg photographs unambiguously demonstrate that $ZrTe_5$ is isostructural with $HfTe_5$. The positional parameters for $ZrTe_5$ must clearly be very similar to those for $HfTe_5$, but no attempt has been made to determine their actual values.

DESCRIPTION AND DISCUSSION OF THE $HfTe_5$ STRUCTURE

Important interatomic distances and angles calculated from the unit cell dimensions and the positional parameters in Table 1 are given in Table 2. Fig. 1 shows the structural arrangement projected along $[100]$. A left hand coordinate system is adopted in order to facilitate comparison with the $ZrSe_3$ type structure (Fig. 2). Apart from the more customary structural merits of such a comparison, this particular one is of considerable interest because $ZrTe_3$ and $HfTe_3$ crystallize with the $ZrSe_3$ type structure.⁹

Table 2. Interatomic distances (<3.5 Å) and angles in the crystal structure of $HfTe_5$. (The standard deviations correspond to those in the positional parameters.)

<i>Interatomic distances (Å)</i>			
Hf—Te _I	2.954(3)	Te _{II} —Te _{II}	2.763(4)
—Te _{II}	2.944(2)	Te _{III} —Te _{III}	2.908(3)
—Te _{III}	2.960(2)		
<i>Interatomic angles (°)</i>			
Te _I —Hf—Te _I	84.57(9)	Hf—Te _I —Hf	84.57(9)
—Te _{II}	88.12(5)		
—Te _{II}	151.09(5)		
—Te _{III}	67.79(4)		
Te _{II} —Hf—Te _{II}	55.97(8)	Hf—Te _{II} —Te _{II}	62.01(4)
—Te _{II}	84.90(7)		
—Te _{II}	110.58(10)		
—Te _{III}	83.55(5)		
—Te _{III}	133.96(4)		
Te _{III} —Hf—Te _{III}	118.53(10)	Hf—Te _{III} —Te _{III}	108.72(9)
		Te _{III} —Te _{III} —Te _{III}	86.20(11)

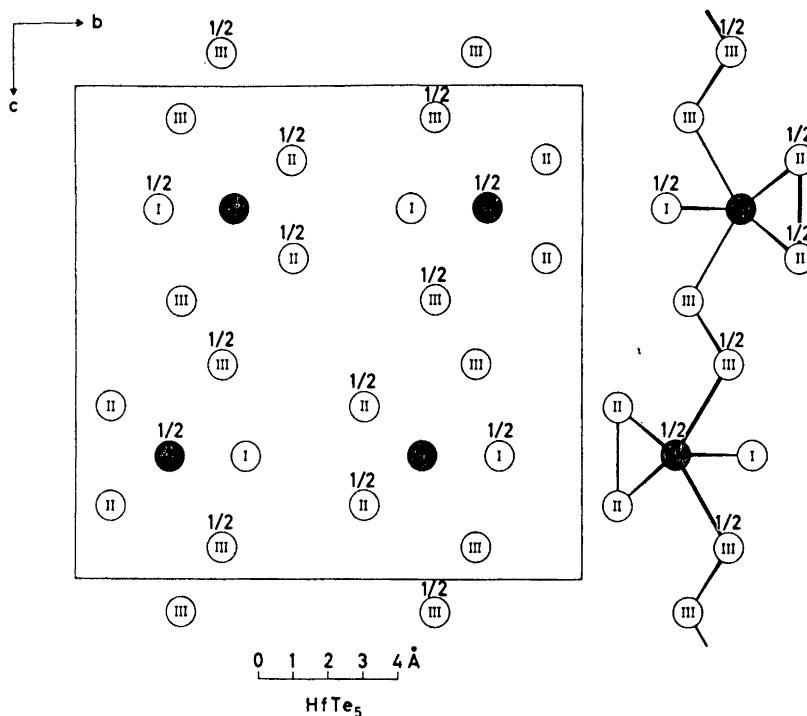


Fig. 1. The crystal structure of HfTe_5 projected along $[100]$. In this and the following diagram filled and open circles represent the metal (T) and non-metal (X) atoms, respectively. The numbers indicate fractions of the projection axis.

Each T atom in the HfTe_5 and ZrSe_3 type structures have nearly identical coordinations of eight close X neighbours. Six X atoms are at the corners of a triangular prism and two lie outside rectangular faces of the prism. These coordination polyhedra (which are distorted variants of the type named bi-capped trigonal prism) are linked together by $X-X$ zig-zag chains (running parallel to $[100]$) in the case of HfTe_5 and by X atoms which belong to neighbouring prisms in ZrSe_3 . The latter distinction accounts for the difference in composition between the two compounds. Moreover, as clearly apparent from Figs. 1 and 2, both structure types consist of distinct layers arranged approximately parallel to (010) and (100) in HfTe_5 and ZrSe_3 , respectively. Each such slab comprises a single sheet of T atoms in the case of HfTe_5 as opposed to the twinned T sheets in the ZrSe_3 type structure. However, despite this dissimilarity in internal architecture, the HfTe_5 and ZrSe_3 slabs are both virtually two dimensional, *i.e.* of infinitesimal thickness in proportion to area. The mutual interactions between adjacent slabs in both structure types are weak as clearly demonstrated by the long interlayer $X-X$ contacts ($\geq 4.161(3)$ Å in HfTe_5 and ≥ 3.87 Å in ZrSe_3 , which are only slightly shorter than the corresponding van der Waals distances of 4.4 Å for $\text{Te}-\text{Te}$ and 4.0 Å for $\text{Se}-\text{Se}$).

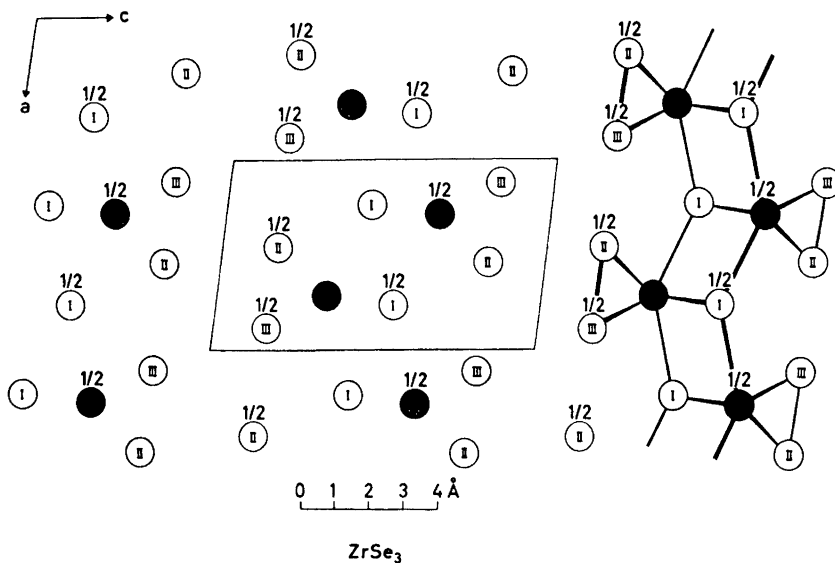


Fig. 2. The crystal structure of ZrSe_3 projected along $[010]$. Data from Krönert and Plieth,⁵ the origin being shifted to $0, \frac{1}{4}, 0$.

Since the X atoms unquestionably play the leading part in compounds of this type their situation must also be discussed in some detail. The three crystallographically non-equivalent X atoms of the HfTe_5 type structure exhibit different immediate surroundings. Each X_I in the HfTe_5 type structure is coordinated to only two T , each X_{II} to two T and another X_{II} , and each X_{III} to one T and two other X_{III} . In the ZrSe_3 type structure each X_I is coordinated to four T and each X_{II} and X_{III} have nearly identical configurations of two T and, respectively, one X_{III} and one X_{II} as near neighbours. Hence, the coordination numbers for the X atoms in these structure types range between two and four, and according to the $T-X-T$ and $X-X-T$ bond angles (in Table 2 for HfTe_5) the corresponding coordination polyhedra may be regarded as distorted tetrahedra with zero, one, or two of the corners vacant. Consequently, each X atom in the two structure types may obtain a complete octet in its valence shell, implying that, apart from X_I of the ZrSe_3 type structure, all X atoms must carry one or two lone electron pairs. The latter deduction is clearly open to future experimental and/or theoretical verification.

In order to form an idea about the valence situation in these compounds it is convenient to test them in terms of the generalized $(8-N)$ rule (*cf.*, *e.g.*, Ref. 10). The correct mathematical formulation of the rule is in this case (*viz.* assuming complete octets on all X atoms) $n + P - Q = 8a$, 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. Most of the compounds with the ZrSe_3 type structure

are diamagnetic semiconductors and all of them satisfy the generalized $(8-N)$ rule with $a=22$, $P=2$, $Q=0$, and $a=3$ (*cf.*, *e.g.*, Ref. 9). ZrTe_5 and HfTe_5 are diamagnetic with temperature dependent susceptibilities as shown in Fig. 3. Hence, and in accordance with previous experience, each T atom is assumed

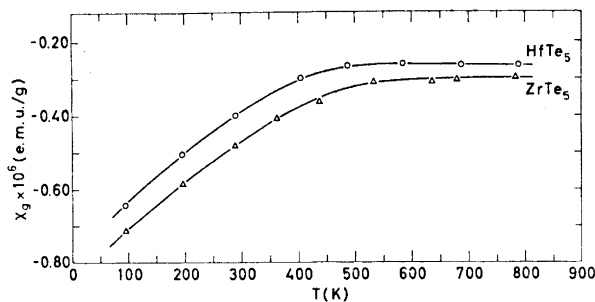


Fig. 3. Magnetic susceptibility *versus* temperature for ZrTe_5 and HfTe_5 . The observations are not corrected for induced diamagnetism.

to contribute 4 electrons and each X atom 6 electrons to $n(=34)$ for ZrTe_5 and HfTe_5 . Neglecting the distinction between the $X_{\text{II}}-X_{\text{II}}$ and $X_{\text{III}}-X_{\text{III}}$ bond lengths in the HfTe_5 type structure (Table 2 and *vide infra*) and assigning a single electron pair to each such bond, the structural data give $P=2+2 \times 2=6$ and $Q=0$. The composition TX_5 (crystallographic formula $\text{TX}_1(\text{X}_{\text{II}}\text{X}_{\text{III}})_2$) yields $a=5$. The values $n=34$, $P=6$, $Q=0$, and $a=5$ show that the generalized $(8-N)$ rule is fulfilled for ZrTe_5 and HfTe_5 . The rule is often used as a necessary, but insufficient criterion for the prediction of semiconduction. Thus, ZrTe_5 and HfTe_5 are potential semiconductors, although this was not brought out in their diffuse reflectance spectra, which show a uniform decrease with increasing wave length apart from a slight irregularity at the long wave length limit. Electrical conductivity measurements on ZrTe_5 and HfTe_5 single crystals will be carried out in order to shed further light on this problem.

The mutual differences between the $\text{Hf}-\text{Te}_I$, $\text{Hf}-\text{Te}_{\text{II}}$, and $\text{Hf}-\text{Te}_{\text{III}}$ bond distances in Table 2 is not significant according to the significance test of Cruickshank.^{11,12} The same applies to the $\text{Zr}-\text{Te}$ bond distances in ZrTe_5 .⁵ This together with the values of the corresponding bond angles lead one to propose d^5sp^2 as the idealized hybridization scheme for the T atoms in these compounds. (The valence bond language is used for convenience, but a similar statement can also be given in terms of the molecular orbital formalism.) No useful explanation can be given, however, as to why these compounds favour this somewhat complex hybridization for the T atoms. The information conveyed by the average $\text{Hf}-\text{Te}$ and $\text{Zr}-\text{Te}$ bond distances of 2.950 and 2.73₈ Å, respectively, cannot be appraised owing to the lack of suitable data for comparison.

The difference between the $\text{Te}_{\text{II}}-\text{Te}_{\text{II}}$ and $\text{Te}_{\text{III}}-\text{Te}_{\text{III}}$ bond distances (Table 2) is to be classified as highly significant. The cause of this distinction

is rather obscure. The $\text{Te}_{\text{II}}-\text{Te}_{\text{II}}$ and $\text{Se}_{\text{II}}-\text{Se}_{\text{III}}$ bond lengths of 2.763(4) and 2.34 Å, respectively, which are analogously situated in the atomic arrangements of HfTe_5 and ZrSe_3 (cf. Figs. 1 and 2), match almost perfectly the single bond (tetrahedral) Te-Te and Se-Se distances (2.74 and 2.34 Å, respectively) listed by Pauling.¹³ The $\text{Te}_{\text{III}}-\text{Te}_{\text{III}}$ bond length of 2.908(3) Å, on the other hand, conforms with the Te-Te distances found in a number of other transition metal polytellurides (e.g. 2.923 Å in TaTe_4 ¹⁴ and 2.926(1) Å in FeTe_2 ¹⁵). The bond distance of 2.835(2) Å in elemental Te falls half way between the values for the $\text{Te}_{\text{II}}-\text{Te}_{\text{II}}$ and $\text{Te}_{\text{III}}-\text{Te}_{\text{III}}$ distances. Further progress in the clarification of this problem is clearly intimately associated with the assessment of the normal, single bond Te-Te distance appropriate to HfTe_5 . This evidently requires data which are not available at present.

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