

## THERMODYNAMICS OF SUBLIMATION AND CRYSTAL CHEMISTRY OF $\text{Tm}_{0.77}\text{Te}$

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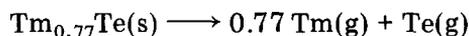
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### Summary

The congruent vaporization of solid  $\text{Tm}_{0.77}\text{Te}$  (rhombohedral, with hexagonal lattice parameters  $a = 430.9$  pm,  $c = 1083.8$  pm) was investigated by the Knudsen effusion weight-loss technique over the temperature range 1624 - 1798 K. Using literature data for the enthalpies of dissociation of gaseous  $\text{TmTe}$  and  $\text{Te}_2$  and for the free energy functions of gaseous  $\text{TmTe}$ ,  $\text{Te}_2$ , thulium and tellurium, it was established that the vaporization to the atoms occurs predominantly according to



while the molecular species  $\text{TmTe}$  and  $\text{Te}_2$  are of minor and very minor importance respectively. The following vapour pressure equation was derived for the vaporization to the atoms:

$$\log K = -(34601 \pm 466) \cdot T^{-1} + (11.46 \pm 0.27)$$

Second and third law calculations based on estimated thermodynamic data for  $\text{Tm}_{0.77}\text{Te}$  yielded the following standard enthalpies and entropies of reaction:

$$\Delta H_{298}^{\circ}(\text{II}) = 681.0 \pm 11.8 \text{ kJ} \cdot \text{mol}^{-1}; \Delta S_{298}^{\circ}(\text{II}) = 241.1 \pm 8.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta H_{298}^{\circ}(\text{III}) = 675.6 \pm 22.1 \text{ kJ} \cdot \text{mol}^{-1}; \Delta S_{298}^{\circ}(\text{III}) = 238 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

A value of  $\Delta_f H_{298}^{\circ} [\text{Tm}_{0.77}\text{Te(s)}] = -279.1 \pm 16.3 \text{ kJ} \cdot \text{mol}^{-1}$  was derived for the standard enthalpy of formation. The crystal chemistry and thermochemical properties of  $\text{Tm}_{0.77}\text{Te}$  are discussed.

### 1. Introduction

In recent years the problem of mixed valency in thulium chalcogenides has stimulated significant research on the solid-state and physical properties

of these compounds, see, for example, ref. 1. Kaldis *et al.* [2] have studied part of the phase diagram of the system Tm–Te. They were able to show that the end phases in this system,  $\text{Tm}^{2+}\text{Te}$  (NaCl-type structure) and  $\text{Tm}_{0.68}^{3+}\text{Te}$  ( $\text{Sc}_2\text{S}_3$  structure, superstructure of NaCl type) have integral valencies. It was concluded that extended solid solutions between these two borderline phases probably do not exist and that the change in the valence of thulium takes place via a miscibility gap, in which the cubic NaCl-type phase coexists with a rhombohedral phase of unknown structure and of composition  $\text{Tm}_{0.80}\text{Te}$ , supposedly containing an appreciable concentration of  $\text{Tm}^{3+}$ . It is noteworthy that the thermochemical properties of the various phases in this system seem to be completely unknown. From studies of the thermodynamics of vaporization of EuTe (Petzel [3]) and of SmTe and YbTe (Petzel and Ludwigs [4]) the standard enthalpies of formation of these monotellurides have been derived with reasonable accuracy. Since the divalent character of the lanthanoids in these compounds is well established for low-pressure conditions and supposedly also holds for thulium in the monotelluride phase, we also considered it feasible to derive the enthalpy of formation of TmTe via a vaporization study. However, preliminary experiments showed that the thermal decomposition of tellurium-rich thulium tellurides *in vacuo* did not yield the monotelluride but led reproducibly to a congruently vaporizing phase with a molar ratio Tm:Te < 1. The results of a detailed investigation on the thermodynamics of vaporization and the crystal chemistry of this phase are presented in this paper.

## 2. Experimental details

### 2.1. Preparation and characterization of compounds

Thulium telluride samples of approximate composition  $\text{TmTe}_{1.5}$  were prepared by reaction of thulium metal (purity, 99.9%, Auer-Remy) with tellurium (purity, 99.999%, Ventron) in outgassed and evacuated silica ampoules at 1150 K and also by reaction of highly pure, practically oxygen-free  $\text{TmF}_3$  with gaseous tellurium and hydrogen at 1250–1300 K. The details of the latter preparative technique have been described in ref. 4.  $\text{TmF}_3$  was prepared from  $\text{Tm}_2\text{O}_3$  (purity, 99.999%, Auer-Remy) by a method described in ref. 5. The more or less inhomogeneous thulium telluride samples were annealed and decomposed in a high vacuum at approximately 1600 K and were then sublimed twice inside a cylindrical molybdenum crucible in a temperature gradient from 1770 to 1700 K. While small amounts of involatile, beige-coloured residues of  $(\text{TmO})_2\text{Te}$  were found after the first sublimation, no residual involatile impurity could ever be detected after the second sublimation. This observation was not unexpected, since the lanthanoid oxide tellurides of composition  $(\text{LnO})_2\text{Te}$ , which, with the exception of  $(\text{EuO})_2\text{Te}$  and  $(\text{YbO})_2\text{Te}$ , are generally formed on contamination of lanthanoid tellurides with oxygen, are indeed very involatile compounds (Petzel and Ludwigs [6]). The doubly sublimed, metallic blue

thulium telluride could hence be considered as practically free of oxygen-containing impurities. It was furthermore concluded that the composition of the sublimed material represented the congruently vaporizing composition under the given conditions of temperature, pressure and crucible material. The purified material, which proved to be extremely sensitive to the oxidative and hydrolytic effects of the atmosphere and had therefore always to be handled under a dry inert gas, was characterized by quantitative analysis of the thulium content and by its X-ray powder pattern (Hägg Guinier chamber, Cu  $K\alpha_1$  radiation, mixture of sample and silicon (NBS 640 A) as internal calibration standard, contained in sealed glass capillaries). The substance proved to be reasonably well crystallized and all reflections could be indexed rhombohedrally with hexagonal lattice parameters  $a = 430.9$  pm and  $c = 1083.8$  pm. The material was analysed for its metal content by the following pyrohydrolytical method, which we have found to be generally suitable for the quantitative decomposition of lanthanoid tellurides. A weighed amount of the telluride, contained in a mullite boat, was pyrohydrolyzed for 3 - 5 h at approximately 1400 K in a stream of hydrogen saturated with water vapour at 323 K. The formation of tellurates is safely prevented by this procedure, and the residue consists only of the pure sesquioxide. The analyses yielded metal contents of  $50.5 \pm 0.2$  wt.% Tm and thus led to the formula  $Tm_{0.77}Te$ . The crystal chemical justification of this formula is discussed in detail in Section 4.1.

## 2.2. Vapour pressure measurements

The vapour pressure measurements were carried out by the Knudsen effusion weight-loss technique. Two cylindrical molybdenum Knudsen cells with effective orifice areas of  $2.5052 \cdot 10^{-3}$  cm<sup>2</sup> (cell A) and  $1.780 \cdot 10^{-3}$  cm<sup>2</sup> (cell B) were used. The cells were heated by radiation from an inductively heated cylindrical tantalum susceptor in a high vacuum ( $p \leq 10^{-5}$  mbar) inside a water-cooled silica tube. The temperature was measured by sighting an optical pyrometer (Leeds and Northrup, type 8632-C) onto a cylindrical black body cavity in the bottom of the cell via an optical window and a prism. The temperature readings were corrected for the insertion of the window and the prism. The effused mass was determined by weighing the cell before and after each experiment and the time was measured with a precision electronic clock. In order to establish a satisfactory accuracy of the temperature measurements, the Knudsen cells were calibrated by measuring vapour pressures of liquid tin (purity, 99.99995%, Ventron). By comparing the experimental results with well-established vapour pressure data from the literature [7], appropriate corrections could be applied to the temperature readings. The accuracy of the temperature measurements was assumed to be  $\pm 5$  K after considering all corrections.

After a total vaporization of 60 mg of  $Tm_{0.77}Te$  the weight change of a molybdenum cell proved to be less than 0.1 mg. It was hence concluded that molybdenum is chemically inert against  $Tm_{0.77}Te$ . That this composition represented in fact a congruently vaporizing composition was confirmed

by the analytical evidence that the metal contents of the starting material and of a residue obtained after extensive vaporization of material were identical within the accuracy limits of the analytical method.

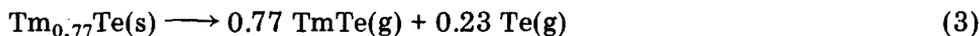
Rates of effusion with a total of 21 data points were measured over the temperature range 1624 - 1798 K; the experimental data are collected in Table 1.

### 3. Thermodynamic evaluation of effusion results

The amount of a gaseous species  $i$ ,  $m_i$  (g) of molar mass  $M_i$  ( $\text{g}\cdot\text{mol}^{-1}$ ) effused in time  $t$  (s) at temperature  $T$  (K) from a Knudsen cell with an orifice of effective area  $a$  ( $\text{cm}^2$ ) is related to the partial pressure of species  $i$ ,  $p_i$  (bar) by the Knudsen equation:

$$p_i = \frac{m_i}{a \cdot t} \cdot \left( \frac{2 \cdot \pi \cdot R \cdot T}{M_i} \right)^{1/2} = \frac{m_i}{a \cdot t \cdot 43.7519} \cdot \left( \frac{T}{M_i} \right)^{1/2} \quad (1)$$

In solid-gas equilibria of lanthanoid telluride systems the gaseous species Ln, Te, LnTe and  $\text{Te}_2$  have to be taken into account under the low total pressures which are a typical condition of Knudsen effusion measurements [8]. Hence, in the congruent vaporization of  $\text{Tm}_{0.77}\text{Te}$ , the following vaporization reactions had to be considered simultaneously for the thermodynamic evaluation of the effusion data:



The equilibrium partial pressures of the various gaseous species occurring in reactions (2) - (4) were calculated from the rates of effusion using the following thermodynamic data: the standard enthalpies of dissociation of TmTe and  $\text{Te}_2$ , 310 and 263  $\text{kJ}\cdot\text{mol}^{-1}$  respectively [9, 10] and the free energy functions of gaseous TmTe, thulium, tellurium and  $\text{Te}_2$  [9 - 11]. The equilibrium partial pressures are summarized in Table 1. It is obvious that the atomic species Tm and Te are predominant, while the molecular species TmTe and  $\text{Te}_2$  are of minor and very minor importance respectively. Therefore, reaction (2) was considered as the main vaporization reaction under the experimental conditions. A plot of  $\log K$  vs.  $T^{-1}$  for reaction (2) is shown in Fig. 1. A linear least-square treatment of the data yielded the following vapour pressure equation for reaction (2) (with standard deviations):

$$\log K = -(34601 \pm 466) \cdot T^{-1} + (11.46 \pm 0.27) \quad (5)$$

From this equation the following values could be derived for the enthalpy and entropy of reaction, related to the median temperature of the measurements, 1711 K:

$$\Delta H_{1711}^\circ = 662.4 \pm 8.9 \text{ kJ}\cdot\text{mol}^{-1}; \Delta S_{1711}^\circ = 219.5 \pm 5.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

TABLE 1

Vaporization data of  $\text{Tm}_{0.77}\text{Te}(s)$ 

$T$ (K)	Rate ( $\text{mg}\cdot\text{h}^{-1}$ )	Cell	$p_{\text{Tm}}$ (bar)	$p_{\text{Te}}$ (bar)	$p_{\text{TmTe}}$ (bar)	$p_{\text{Te}_2}$ (bar)	$K^a$ reaction (2)	$\Delta H_{298}^{\circ}(\text{III})$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )
1624	0.75	A	2.6201 E-6	3.0490 E-6	4.8832 E-7	5.2202 E-9	1.516 E-10	675.0
1653	1.15	A	4.0232 E-6	4.6833 E-6	7.6264 E-7	8.7132 E-9	3.239 E-10	676.4
1659	1.33	A	4.6258 E-6	5.3942 E-6	9.3092 E-7	1.0778 E-8	4.154 E-10	675.4
1684	1.99	A	6.9159 E-6	8.0792 E-6	1.4792 E-6	1.8151 E-8	8.477 E-10	675.4
1692	2.34	A	8.0893 E-6	9.4666 E-6	1.8259 E-6	2.2777 E-8	1.121 E-9	674.6
1708	2.77	A	9.6684 E-6	1.1300 E-5	2.1090 E-6	2.7184 E-8	1.534 E-9	676.4
1713	3.00	A	1.0469 E-5	1.2240 E-5	2.3098 E-6	3.0197 E-8	1.767 E-9	676.3
1716	2.18	B	1.0736 E-5	1.2546 E-5	2.3372 E-6	3.0702 E-8	1.846 E-9	676.8
1723	3.69	A	1.2773 E-5	1.4971 E-5	3.0379 E-6	4.0525 E-8	2.518 E-9	675.0
1725	2.64	B	1.2897 E-5	1.5110 E-5	3.0196 E-6	4.0395 E-8	2.561 E-9	675.6
1726	4.00	A	1.3774 E-5	1.6167 E-5	3.4072 E-6	4.5760 E-8	2.882 E-9	674.3
1736	4.16	A	1.4538 E-5	1.7015 E-5	3.3261 E-6	4.5541 E-8	3.162 E-9	676.7
1741	3.13	B	1.5422 E-5	1.8048 E-5	3.5183 E-6	4.8584 E-8	3.509 E-9	677.1
1742	3.14	B	1.5493 E-5	1.8127 E-5	3.5070 E-6	4.8192 E-8	3.537 E-9	677.4
1756	5.88	A	2.0379 E-5	2.3927 E-5	5.1095 E-6	7.2981 E-8	5.765 E-9	675.5
1758	6.21	A	2.1440 E-5	2.5198 E-5	5.5260 E-6	7.9273 E-8	6.313 E-9	675.0
1770	5.36	B	2.5943 E-5	3.0539 E-5	6.9831 E-6	1.0290 E-7	8.859 E-9	674.4
1772	5.45	B	2.6419 E-5	3.1093 E-5	7.0698 E-6	1.0450 E-7	9.147 E-9	674.7
1776	8.56	A	2.9234 E-5	3.4484 E-5	8.2790 E-6	1.2340 E-7	1.097 E-8	673.5
1783	6.36	B	3.0794 E-5	3.6275 E-5	8.4502 E-6	1.2723 E-7	1.201 E-8	674.8
1798	7.16	B	3.5111 E-5	4.1272 E-5	9.1582 E-6	1.4182 E-7	1.511 E-8	676.8

<sup>a</sup> Standard state pressure =  $p^{\circ} = 0.1013 \text{ MPa}$ .

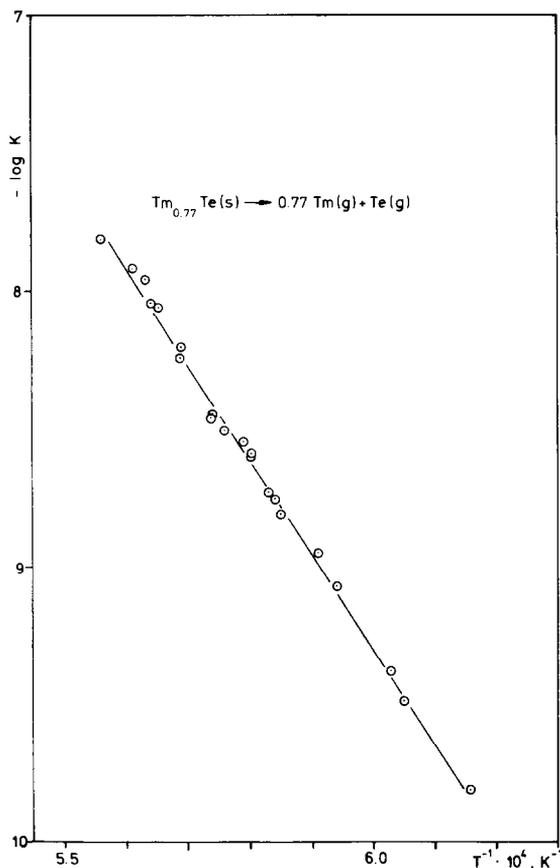


Fig. 1. Plot of  $\log K$  vs.  $T^{-1}$  for the reaction  $\text{Tm}_{0.77}\text{Te}(\text{s}) \rightarrow 0.77 \text{Tm}(\text{g}) + \text{Te}(\text{g})$ .

The most important thermodynamic quantity, which can be derived from the results for reaction (2), is the standard enthalpy of formation of solid  $\text{Tm}_{0.77}\text{Te}$ . In order to gain this information, the enthalpy of vaporization had first to be extrapolated to 298 K by the second and third law methods. Since no thermodynamic data are known for  $\text{Tm}_{0.77}\text{Te}$ , its standard entropy  $S_{298}^{\circ}$  and the enthalpy and entropy increments,  $(H_T^{\circ} - H_{298}^{\circ})$  and  $(S_T^{\circ} - S_{298}^{\circ})$  respectively, were estimated as follows. By subtracting from the estimated standard entropy of  $\text{Tm}_{0.67}\text{Te}$ ,  $84.7 \pm 6.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  [10], the entropy contribution of 0.13 mol of  $\text{Te}^{2-}$  ion,  $6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  [12], a value of  $S_{298}^{\circ} [\text{Tm}_{0.77}\text{Te}(\text{s})] = 90.7 \pm 6.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  was obtained. The enthalpy and entropy increments were assumed to be equal to one quarter of the measured and in part extrapolated sums of the data for  $\text{Nd}_2\text{Te}_3$  and  $\text{NdTe}$  [9]. All estimated thermodynamic data for  $\text{Tm}_{0.77}\text{Te}$  are collected in Table 2. The second law data extrapolation (index II) yielded the following results for reaction (2):

$$\Delta H_{298}^{\circ}(\text{II}) = 681.0 \pm 11.8 \text{ kJ} \cdot \text{mol}^{-1} \quad \Delta S_{298}^{\circ}(\text{II}) = 241.1 \pm 8.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

TABLE 2

Estimated thermodynamic data of  $\text{Tm}_{0.77}\text{Te}(\text{s})$ 

$T$ (K)	$H_T^\circ - H_{298}^\circ$ ( $\text{J}\cdot\text{mol}^{-1}$ )	$S_T^\circ - S_{298}^\circ$ ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )	$-\text{fef}$ ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )
1600	65 435	83.0	132.8
1700	70 819	86.2	135.3
1800	76 261	89.2	137.6

The third law enthalpies (index III) for reaction (2), calculated for each data point, and the  $K$  values are also collected in Table 1. The average third law enthalpy and the third law entropy are

$$\Delta H_{298}^\circ(\text{III}) = 675.6 \pm 22.1 \text{ kJ}\cdot\text{mol}^{-1} \quad \Delta S_{298}^\circ(\text{III}) = 238.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The error limits of the second law results are the sums of the standard deviations and an assumed 15% error of the reduction to 298 K. The error limits of the third law enthalpy were found by adding a 5% error in  $\Delta\text{fef}$  to the standard deviation. Despite the necessity for extensive data estimations a satisfactory agreement between the second and third law results is obvious. Since the third law enthalpies calculated for the individual data points do not show a noticeable dependence on temperature, it can be concluded with certain reservations that the experimental results and the estimated data are both reasonably accurate.

Using  $\Delta_f H_{298}^\circ(\text{Tm}(\text{g})) = 247.3 \pm 4.2 \text{ kJ}\cdot\text{mol}^{-1}$  [9] and  $\Delta_f H_{298}^\circ(\text{Te}(\text{g})) = 211.7 \pm 1.3 \text{ kJ}\cdot\text{mol}^{-1}$  [10] and the second law standard enthalpy for reaction (2),  $681.0 \pm 11.8 \text{ kJ}\cdot\text{mol}^{-1}$ , we finally obtained a value of  $-279.1 \pm 16.3 \text{ kJ}\cdot\text{mol}^{-1}$  as the standard enthalpy of formation of  $\text{Tm}_{0.77}\text{Te}$ .

## 4. Discussion

The occurrence of a congruently vaporizing composition  $\text{Tm}_{0.77}\text{Te}$  and the crystal chemistry and thermochemical properties of this compound seem to be especially worthy of discussion.

### 4.1. Crystal chemistry of $\text{Tm}_{0.77}\text{Te}$

The Guinier X-ray powder patterns of  $\text{Tm}_{0.77}\text{Te}$  revealed a slightly distorted halite structure as judged from splitting of two-thirds of the parent structure reflections, see Table 3. Neglecting this splitting, we obtain a lattice parameter of  $a_c = 614.79 \text{ pm}$  for the undistorted NaCl structure. Crystallographic data of this hypothetical parent structure are listed on the left side of Table 3.

It is worthwhile to mention that the rare earth tellurides, crystallizing in the NaCl-type or related structures, have generally strong reflections for  $hkl$  all even, while the reflections for  $hkl$  all odd are very weak and in many

TABLE 3

X-ray powder diffraction data of  $\text{Tm}_{0.77}\text{Te}$ 

<i>NaCl-type parent structure (hypothetical)</i>			<i>Rhombohedral basis structure (observed)</i>			
<i>h k l</i>	<i>I</i>	<i>d</i> (pm)	<i>d</i> <sub>calc</sub> (pm)	<i>d</i> <sub>obs</sub> (pm)	<i>I</i>	<i>h k l</i>
1 1 1	0	354.9	{ 361.3 352.8	— —	0 0	0 0 3 1 0 1
2 0 0	<i>st</i>	307.4	307.35	307.48	<i>vst</i>	0 1 2
2 2 0	<i>st</i>	217.4	{ 219.26 215.45	219.22 215.38	<i>st</i> <i>st</i>	1 0 4 1 1 0
3 1 1	0	185.4	{ 187.44 185.04 183.88	— — —	0 0 0	0 1 5 1 1 3 0 2 1
2 2 2	<i>st</i>	177.5	{ 180.64 176.42	180.54 176.53	<i>w</i> <i>st</i>	0 0 6 2 0 2
4 0 0	<i>st</i>	153.7	153.67	153.66	<i>w</i>	0 2 4
3 3 1	0	141.0	{ 143.01 141.41 139.86	— — —	0 0 0	1 0 7 2 0 5 2 1 1
4 2 0	<i>st</i>	137.5	{ 138.42 136.50	138.44 136.46	<i>st</i> <i>st</i>	1 1 6 1 2 2
4 2 2	<i>st</i>	125.5	{ 127.35 125.11 124.39	127.37 125.11 124.39	<i>vw</i> <i>w</i> <i>w</i>	0 1 8 2 1 4 3 0 0
<i>Fm</i> 3 <i>m</i> , <i>Z</i> = 4			<i>R</i> 3̄, <i>Z</i> = 3			
<i>a</i> = 614.79 pm			<i>a</i> = 430.90(7) pm			
<i>V</i> = 2.3237 · 10 <sup>8</sup> pm <sup>3</sup>			<i>c</i> = 1083.8(2) pm			
<i>V'</i> = <i>V</i> / <i>Z</i> = 5.8092 · 10 <sup>7</sup> pm <sup>3</sup>			<i>V</i> = 1.7428(5) · 10 <sup>8</sup> pm <sup>3</sup>			
			<i>V'</i> = <i>V</i> / <i>Z</i> = 5.8092(2) · 10 <sup>7</sup> pm <sup>3</sup>			

cases not even detectable. This phenomenon led us to choose a parent unit cell with  $a_c = 614.79$  pm and not with  $a'_c = a_c/2 = 307.4$  pm, although such a choice would also have been formally possible. Furthermore, the volume of the latter cell,  $2.9048 \cdot 10^7$  pm<sup>3</sup>, would be too small to accommodate two different atoms, as requested for  $\text{Tm}_{0.77}\text{Te} \equiv \text{Tm}_{0.77}\square_{0.23}\text{Te}$ . The alternative formula,  $\text{TmTe}_{1.30}$ , should be ruled out in view of the crystal chemistry of halite, according to which the incorporation of interstitial anions in such a high concentration is impossible. Analysis of the splitting of the parent structure reflections leads to a symmetry reduction from cubic to rhombohedral. The crystallographic data of this actual structure are listed on the right side of Table 3. The parent unit cell with three formula units in the hexagonal cell represents the smallest so-called basis structure of halite. The observed lattice parameter  $c = 1083.8$  pm is somewhat larger than

the corresponding halite diagonal  $\sqrt{3} \cdot a_c = 1064.8$  pm, while  $a = 430.90$  pm is smaller than  $0.5 \cdot \sqrt{2} \cdot a_c = 434.72$  pm. Generally, distortions of a parent structure caused by ordering of lattice defects call for the appearance of superstructure reflections. We could not find any evidence for them on our powder patterns. Therefore we prefer to rely on the above-mentioned basis structure until a superstructure is found using different techniques, e.g. single crystal X-ray work and electron or neutron diffraction.

Kaldis *et al.* [2] also reported a rhombohedral cell with  $a = 862.0$  pm,  $c = 1081.2$  pm, corresponding to a  $2 \times 2 \times 1$  superstructure of our basis structure but related to the composition  $\text{Tm}_{0.80}\text{Te}$ ; their results are in accordance with the work of Iandelli and Palenzona [13]. It is not clear from the published data whether or not the lattice parameter  $a$  has been chosen according to actually observed superstructure reflections. Obviously, a reduction of their cell results in  $a_b = 0.5 \cdot a_s = 431.0$  pm and  $c = 1081.2$  pm, which is in very good agreement with our findings. However, the discrepancy in the analytical data,  $\text{Tm}_{0.77}\text{Te}$  (this work) *vs.*  $\text{Tm}_{0.80}\text{Te}$  (ref. 2) is apparently outside the range of experimental error. We believe that our analytical result is closer to the true situation for the following reason. According to the conclusions of Kaldis *et al.* [2] this phase should be considered as a compound intermediate between  $\text{Tm}^{2+}\text{Te}^{2-}$  (NaCl structure with  $a_c = 635.9$  pm,  $Fm\bar{3}m$ ,  $Z = 4$ ,  $V' = V/Z = 6.4284 \cdot 10^7$  pm<sup>3</sup>) and  $\text{Tm}_2^{3+}\text{Te}_3^{2-} \equiv \text{Tm}_{0.667}\text{Te}$  (experimental composition  $\text{Tm}_{0.68}\text{Te}$ , isostructural to  $\text{Sc}_2\text{S}_3$  [14], with the following structural data: orthorhombic  $Fddd$ ,  $a = 1206.0$  pm  $\approx 2a_c$ ,  $b = 854.1$  pm  $\approx \sqrt{2} \cdot a_c$ ,  $c = 2563.1$  pm  $= 3 \cdot \sqrt{2} \cdot a_c$ ,  $Z = 48$ ,  $a_c = 603.9$  pm,  $V' = V/Z = 5.5022 \cdot 10^7$  pm<sup>3</sup>), containing both  $\text{Tm}^{2+}$  and  $\text{Tm}^{3+}$  ions in a well-defined ratio. Since both end members of the system  $\text{Tm}-\text{Te}$ ,  $\text{Tm}^{2+}\text{Te}$  and  $\text{Tm}^{3+}\text{Te}_3$ , have the halite and a halite-related structure respectively, we should be able to correlate the observed formula volumes unambiguously with the analytical compositions. A plot of formula volume *vs.* composition in Fig. 2 reveals that the observed formula volume for the composition  $\text{Tm}_{0.77}\text{Te}$ ,  $5.8092 \cdot 10^7$  pm<sup>3</sup> indeed fits satisfactorily with the linear interpolation between the data for  $\text{TmTe}$  and  $\text{Tm}_2\text{Te}_3$ . Therefore the conclusion that both valencies contribute in a relation of  $\text{Tm}^{3+}:\text{Tm}^{2+} = 3:2$  to the total thulium content of  $\text{Tm}_{0.77}\text{Te}$  seems to be well justified. Hence, at this state of knowledge, the best formula to describe the crystal chemistry of this compound is  $\text{Tm}_{0.46}^{3+}\text{Tm}_{0.31}^{2+}\square_{0.23}\text{Te}_{1.00}^{2-}$ .

In addition, there exists with respect to the formula  $\text{Tm}_{0.77}\text{Te}$  a striking similarity to the blue compound  $\text{Tm}_{0.76}\text{Se}$ , the structure of which has been investigated by Siegrist *et al.* [15]. The structure of this selenide is also derived from halite. Although no splitting of the parent reflections could be observed, the true symmetry is orthorhombic  $Pnnn$ , as derived from superstructure reflections and atomic parameters. The superstructure is caused by ordering of cation vacancies and relaxation of neighbouring anions. On the evidence of diffraction data,  $\text{Tm}_{0.77}\text{Te}$  and  $\text{Tm}_{0.76}\text{Se}$  are not isostructural, although a close structural resemblance between both blue phases does certainly exist.

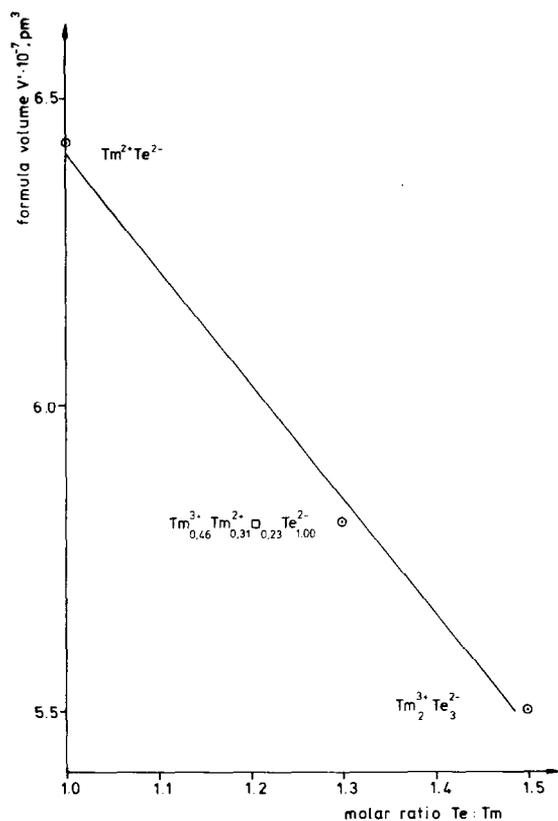


Fig. 2. Plot of formula volumes *vs.* composition for the system  $\text{TmTe}-\text{Tm}_2\text{Te}_3$ .

#### 4.2. Thermochemistry of $\text{Tm}_{0.77}\text{Te}$

Considering the apparent lack of experimentally determined thermochemical data for the various phases in the chalcogenide systems of those lanthanoid elements, for which di- and trivalency is typical, it is very difficult to predict reliably the congruently vaporizing composition of a given lanthanoid-chalcogen system. Neglecting the enthalpies of dissociation of the gaseous monochalcogenides, the thermodynamic stability of the divalent oxidation state of the cation in the condensed phase and the radius of the chalcogenide ion both influence the congruently vaporizing composition. Since it is well established that in predominantly ionic structures the lower oxidation state of the cation becomes more stable as the size of the anion is increased, we should expect that for a given lanthanoid element the congruently vaporizing composition in the oxide system tends to the formula  $\text{LnO}_{1.5}$  ( $\text{Ln}_2\text{O}_3$ ), while for the telluride system it tends to the composition  $\text{LnTe}$ . For samarium, for which the oxidation state 2+ is not easily attained, this situation is clearly observed. The congruently vaporizing compositions are  $\text{SmO}_{1.5}$  [16],  $\text{SmS}_{1.33}$  [17] and  $\text{SmTe}_{1.0}$  [4]. For europium the tendency to be divalent is much more pronounced and the respective

compositions are  $\text{EuO}_{1.5}$  [16, 17, 19],  $\text{EuS}_{1.0}$  [20],  $\text{EuSe}_{1.0}$  [21] and  $\text{EuTe}_{1.0}$  [3]. In contrast, for thulium the divalent state is much less stable than for samarium and it is therefore not unreasonable to expect a congruently vaporizing composition, which even in the telluride system tends to a molar ratio  $\text{Tm}:\text{Te} < 1$ . From the good reproducibility of the effusion results for  $\text{Tm}_{0.77}\text{Te}$  we are indeed inclined to conclude that this composition is representative of the thermodynamic equilibrium situation, at least under the experimental conditions outlined in this paper.

Because of the above-mentioned scarcity of reliable experimental data concerning the enthalpies of formation of the lanthanoid chalcogenides in general, it is difficult to prove that the value of the enthalpy of formation of  $\text{Tm}_{0.77}\text{Te}$ , as derived from the vapour pressure results of this work, represents a reasonable thermochemical quantity. As, formally, the composition  $\text{Tm}_{0.77}\text{Te} \equiv \text{Tm}_3\text{Te}_{3.90}$  is close to the formula  $\text{Ln}_3\text{Te}_4$ , it can be argued that the enthalpy of formation could probably be close to the sum of the respective enthalpies for  $\text{Ln}_{0.67}\text{Te} \equiv \text{Ln}_2\text{Te}_3$  and  $\text{LnTe}$ . Since for  $\text{Ln} \equiv \text{Tm}$  only estimated data are available, the experimental enthalpies of formation of  $\text{YbTe}$ ,  $-376.1 \pm 16.9 \text{ kJ}\cdot\text{mol}^{-1}$  [4] and of  $\text{La}_2\text{Te}_3$ ,  $-784.5 \pm 25.5 \text{ kJ}\cdot\text{mol}^{-1}$  [22], are tentatively taken as more or less representative of  $\text{LnTe}$  and  $\text{Ln}_2\text{Te}_3$  in general. Hence an enthalpy of formation of about  $-1161 \pm 42 \text{ kJ}\cdot\text{mol}^{-1}$  should be expected for  $\text{Ln}_3\text{Te}_4$ , which agrees reasonably well with the value of  $-1088 \pm 64 \text{ kJ}\cdot\text{mol}^{-1}$  derived in this work for the formal composition  $\text{Tm}_3\text{Te}_{3.90}$ .

## References

- 1 P. Wachter and H. Boppart (eds.), *Valence Instabilities*, North-Holland, Amsterdam, 1982.
- 2 E. Kaldis, E. Jilek and H. Spychiger, *J. Less-Common Met.*, 93 (1983) 399.
- 3 T. Petzel, *High Temp. Sci.*, 6 (1974) 246.
- 4 T. Petzel and J. Ludwigs, *High Temp. Sci.*, 24 (1987) 79.
- 5 T. Petzel, *J. Less-Common Met.*, 108 (1985) 241.
- 6 T. Petzel and J. Ludwigs, *J. Less-Common Met.*, 128 (1987) 241.
- 7 C. B. Alcock, V. P. Itkin and M. K. Horrigan, *Can. Metall. Q.*, 23 (1984) 309.
- 8 S. I. Nagai, M. Shinmei and T. Yokokawa, *J. Inorg. Nucl. Chem.*, 36 (1974) 1904.
- 9 S. P. Gordienko, B. V. Fenochka and G. Sh. Viksman, *Thermodynamics of Lanthanoid Compounds*, Naukova Dumka, Kiev, 1979.
- 10 K. C. Mills, *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides*, Butterworths, London, 1974.
- 11 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements*, American Society for Metals, Metals Park, OH, 1973.
- 12 O. Kubaschewski and C. B. Alcock, *Metallurgical Thermochemistry*, 5th edn., Pergamon, Oxford, 1979.
- 13 A. Iandelli and A. Palenzona, *Colloq. Int. CNRS sur les Dérivés Semimétalliques, Orsay, 1965*, Centre National de la Recherche Scientifique, Paris, 1967, p. 397.
- 14 J. P. Dismukes and J. G. White, *Inorg. Chem.*, 3 (1964) 1220; 4 (1965) 970.
- 15 T. Siegrist, Y. Le Page and F. Holtzberg, *J. Less-Common Met.*, 132 (1987) 243.
- 16 M. B. Panish, *J. Chem. Phys.*, 34 (1961) 1079.

- 17 F. Holtzberg and M. A. Frisch, *Rev. Chim. Min.*, 10 (1973) 355.
- 18 J. M. Haschke and H. A. Eick, *J. Chem. Phys.*, 73 (1969) 374.
- 19 J. M. Haschke and H. A. Eick, *J. Chem. Phys.*, 72 (1968) 4235.
- 20 A. V. Hariharan and H. A. Eick, *High Temp. Sci.*, 3 (1971) 123.
- 21 A. V. Hariharan and H. A. Eick, *J. Chem. Thermodyn.*, 6 (1974) 373.
- 22 K. A. Sharifov, Z. S. Karaev and T. K. Azizov, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 3 (1967) 719.