Thermodynamics of $SmCl_3$ and $TmCl_3$: Experimental Enthalpy of Fusion and Heat Capacity. Estimation of Thermodynamic Functions up to 1300 K

L. Rycerz[a,b] and M. Gaune-Escard[b]

[a] Institute of Inorganic Chemistry and Metallurgy of Rare Elements, University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wrocław, Poland

[b] Université de Provence, IUSTI, CNRS UMR 6595, Technopôle de Château Gombert, 5 rue Enrico Fermi, 13453 Marseille Cedex 13, France

Reprint requests to M. G.-E.; Fax: +33 (0)4 91 11 74 39; E-mail: mge@iusti.univ-mrs.fr

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Heat capacities of solid $SmCl_3$ and $TmCl_3$ were measured by differential scanning calorimetry in the temperature range from 300 K up to the respective melting temperatures. The heat capacity of liquid $SmCl_3$ was also investigated. These results were compared with literature data and fitted by a polynomial temperature dependence. The temperature coefficients were given. Additionally, the enthalpy of fusion of $SmCl_3$ was measured. Furthermore, by combination of these results with the literature data on the entropy at 298.15 K, $S^0_m(LnCl_3, s, 298.15\ K)$ and the standard molar enthalpy of formation of $\Delta_{form}H^0_m(LnCl_3, s, 298.15\ K)$, the thermodynamic functions were calculated up to T = 1300 K.

Key words: Samarium Chloride; Thulium Chloride; Heat Capacity; Enthalpy; Entropy; Formation; Fusion; Differential Scanning Calorimetry.

Introduction

The enthalpies of phase transitions of lanthanide chlorides as well as the heat capacities of $LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $GdCl_3$, $DyCl_3$, and $EuCl_3$ have been measured and reported previously [1 - 3]. This work continues an investigation program on lanthanide halides. It presents results of enthalpies of phase transitions and specific heat capacity measurements of the pure lanthanide chlorides $SmCl_3$ and $TmCl_3$ performed with a SETARAM DSC 121 differential scanning calorimeter. The results are compared with original literature data and with literature estimations.

Experimental

Sample Preparation

Thulium chloride ($TmCl_3$) was prepared from the oxide of 99.9% purity, supplied by Merck, by chlorinating with ammonium chloride (POCh Gliwice, Poland – pure for analysis). The synthesis included the following steps:

- preparation of a mixture in the molar ratio Tm_2O_3 : NH_4Cl = 1 : 9,
- sintering and chlorinating under vacuum at 600 K during 3 hours,
- sublimation of unreacted ammonium chloride at 640 K under vacuum,
- melting of crude thulium chloride,
- purification of crude chloride by distillation under reduced pressure (∼0.1 Pa).

As the product after sintering chlorinating and melting was contamined by oxychloride, TmOCl, the next step of preparation was a double distillation of the crude $TmCl_3$ from the less volatile residue (mainly TmOCl). Details of the distillation procedure have been described in [4].

However, this method should not be used for the synthesis of $SmCl_3$ because of the decomposition tendency of this compound. Thus samarium trichloride was prepared by chlorinating the oxide (Merck, 99.9%) with a current of high purity argon (water and oxygen content less than 2 and 0.5 ppmV, respectively) saturated with $SOCl_2$ vapour in a quartz reactor, at 793 - 813 K for 24 hours. This procedure,

Table 1. Chemical analysis of the lanthanide trichlorides.

Compound	$Cl_{observed}$ mass %	$Cl_{theoretical}$ mass %	$Ln_{observed}$ mass %	$Ln_{theoretical}$ mass %
$SmCl_3$	41.44	41.43	58.56	58.57
$TmCl_3$	38.62	38.63	61.38	61.37

which revealed satisfactory, was developed empirically, and no attempt was made to reduce the duration of the chlorinating cycle, although this may be possible.

The chemical analysis of the synthesised lanthanide chlorides was performed by titration methods for the chloride (mercurimetric) and lanthanide (complexometric). The results are presented in Table 1.

All handling of lanthanide chlorides was performed in an argon glove box (water content less than 2 ppmV). Continuous argon purification was achieved by forced recirculation through external molecular sieves.

Differential Scanning Calorimeter (DSC)

The enthalpies of phase transitions and heat capacities were measured with a SETARAM DSC 121 differential scanning calorimeter. The apparatus and the measurements procedure were described in details in [1 - 3].

Measurements

Quartz cells (7 mm diameter and 15 mm long) were filled with the lanthanide chlorides in a glovebox, sealed under vacuum and then placed into the DSC 121 calorimeter.

Enthalpy of transition measurements were carried out with heating and cooling rates between 1 and 5 K min^{-1}.

The so-called "step method", used for C_p measurements, was already described in [1, 2]. In this method, small heating steps are followed by isothermal equilibrations. Two correlated experiments should be carried out to determine the heat capacity of the sample. The first one, with two empty containers of identical mass, and the second one with one of these loaded with the sample. The heat flux is recorded as a function of time and temperature in both runs. The difference of heat flux in both runs is proportional to the amount of heat (Q_i) necessary to increase the temperature of the sample by a small temperature increment ΔT_i. Therefore the heat capacity of the sample is

$$C^0_{p,m} = (Q_i \cdot M_s)/(\Delta T_i \cdot m_s),$$

where m_s is the mass of the sample and M_s the molar mass of the sample.

The same operating conditions (e. g. initial and final temperatures, temperature increment, isothermal delay and heating rate) are required for the two experimental runs. The original SETARAM program performs all necessary calculations.

The heat capacity measurements were performed by the "step method". Each heating step of 5 K was followed by 400 s isothermal delay. The heating rate was 1.5 K min^{-1}. All experiments were started at 300 K and were performed up to 1100 K. The mass difference of the quartz cells in a particular experiment did not exceed 1 mg (mass of the cells: 400 - 500 mg). The mass of the samples was 200 - 500 mg.

Results and Discussion

Enthalpy of Phase Transition

The enthalpy of fusion was determined for $SmCl_3$. As supercooling was observed in DSC cooling curves (about 19 K), the temperature and fusion enthalpy were determined from heating thermograms.

The temperature and fusion enthalpy of $TmCl_3$ have been obtained earlier [1] by Calvet high-temperature microcalorimetry, since the high melting temperature was beyond the experimental range of the DSC 121 apparatus.

$SmCl_3$

$SmCl_3$ was found to melt at 950 K with a corresponding enthalpy and entropy of fusion $\Delta_{fus}H^0_m$ = 47.6 k J mol^{-1} and $\Delta_{fus}S^0_m$ = 50.3 J mol^{-1} K^{-1}, respectively. Our measured melting temperature of $SmCl_3$ agrees well with that measured by Polyachenok and Novikov [5] and that selected by Pankratz [6], although by about 5 K lower than other and older literature data [7].

$TmCl_3$

$TmCl_3$ melts at 1092 K with a corresponding enthalpy and entropy of fusion $\Delta_{fus}H^0_m$ = 35.6 k J mol^{-1} and $\Delta_{fus}S^0_m$ = 32.6 J $mol^{-1}K^{-1}$, respectively [1]. The melting temperature and fusion enthalpy agree well with the reference data of Thoma [8], but this melting

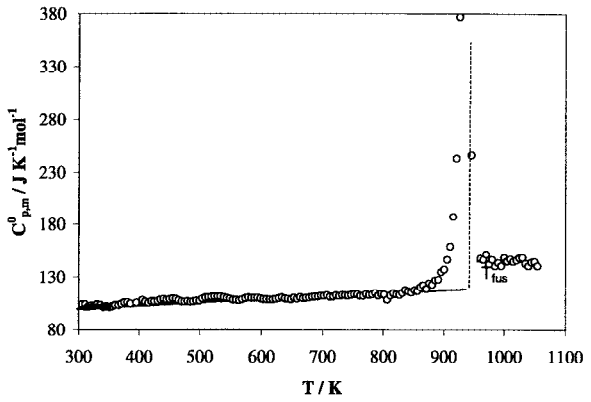

Fig. 1. Molar heat capacity of $SmCl_3$. Open circles: experimental values, black circles: low-temperature data of Sommers and Westrum [10], solid line: polynomial fitting of experimental values.

Table 2. The calculated thermodynamic functions of $SmCl_3$ at selected temperatures from 298.15 to 1300 K.

T / K	$C_{p,m}$	S^0_m	$-(G-H_{298.15})/T$	H_T-H_{298}	$\Delta_{form}H^0_m$	$\Delta_{form}G^0_m$
	— J K^{-1}mol^{-1} —			— kJ mol^{-1} —		
298.15	99.54	150.12	150.12	0.00	−1025.3	−949.6
300	99.60	150.74	150.12	0.18	−1025.3	−949.1
400	102.68	179.82	154.07	10.30	−1023.5	−924.0
500	105.66	203.05	161.62	20.72	−1022.0	−899.3
600	108.61	222.57	170.19	31.43	−1020.6	−874.9
700	111.54	239.54	178.91	42.44	−1019.2	−850.7
800	114.47	254.62	187.45	53.74	−1017.6	−826.8
900	117.39	268.27	195.68	65.33	−1016.0	−803.0
950	118.84	274.66	199.67	71.24	−1015.1	−791.2
950	145.26	324.96	199.67	118.84	−967.5	−791.2
1000	145.26	332.41	206.12	126.10	−965.3	−782.0
1100	145.26	346.25	218.22	140.63	−961.0	−763.9
1190	145.26	357.68	228.33	153.70	−957.1	−747.9
1190	145.26	357.68	228.33	153.70	−960.2	−747.9
1200	145.26	358.89	229.41	155.15	−959.8	−746.1
1300	145.26	370.52	239.81	169.68	−955.5	−728.5

temperature is by about 9 K lower than other literature data [9].

Heat Capacity

$SmCl_3$

Our experimental heat capacity values of $SmCl_3$ are plotted against temperature in Fig. 1 together with the only existing literature data at low temperatures [10]. A very good agreement is observed in this narrow temperature range where comparison is possible. At higher temperatures it was only possible to compare our experimental C_p data for solid $SmCl_3$ with several estimations available in literature. They agree very well with Pankratz [6] and Knacke et al. [11] estimations. The latter estimations replaced previous computations by the same authors [12, 13] that reported alternately lower (up to about 450 K) and larger (starting from 650 K) heat capacities. The heat capacity of liquid $SmCl_3$ was also estimated by the previous authors [6, 11] as $C^0_{p,m}$ = 142.2 J K^{-1}mol^{-1} and 143.5 J K^{-1}mol^{-1} [13].

Our experimental heat capacity data for the liquid were averaged to the constant value $C^0_{p,m}$ = 145.3 J K^{-1}mol^{-1}, i.e. in good agreement with all estimations.

The polynomial heat capacity dependence on temperature used by Barin et al. [12] for lanthanide chlorides,

$$C^0_{p,m} = a + b * 10^{-3}T + c * 10^5T^{-2}, \qquad (1)$$

was also used by us to fit experimental data for solid $SmCl_3$. Because of the good agreement between the low temperature data sets, the contraint that $C^0_{p,m}$(298.15 K) is equal to the reported literature value [10] was introduced to this fitting. However, because of the strong C_p increase when approaching melting, only those data corresponding to a smooth heat capacity dependence on temperature were used.

The thermodynamic functions of samarium trichloride were calculated up to 1300 K using our experimental melting temperature and enthalpy together with heat capacity data. The standard entropy $S^0_m(SmCl_3, s, 298.15\ K)$ = 150.12 J K^{-1}mol^{-1} was taken from [10].

The $C^0_{p,m} = f(T)$ equation was then used to calculate the heat capacity $C^0_{p,m}(T)$ in J K^{-1}mol^{-1}, enthalpy increments $H^0_m(T) - H^0_m(298.15\ K)$ in kJ mol^{-1}, entropy $S^0_m(T)$ and Gibbs energy functions $(G^0_m(T) - H^0_m(298.15))/T$ in J K^{-1}mol^{-1}, both for solid and liquid $SmCl_3$. The corresponding equations are given below. The results for selected temperatures are presented in Table 2.

$SmCl_3$ solid, 298.15 K < T < 950 K:

$$C^0_{p,m} = 91.27 + 29.068*10^{-3}T - 0.351*10^5T^{-2},$$

$$H^0_m(T) - H^0_m(298.15) = 91.27*10^{-3}T + 14.534*10^{-6}T^2 + 0.351*10^2T^{-1} - 28.62,$$

$$S^0_m(T) = 91.27 \ln T + 29.068*10^{-3}T + 0.175*10^5T^{-2} - 378.75,$$

$$-(G^0_m(T) - H^0_m(298.15))/T = 91.27 \ln T + 14.534{*}10^{-3}T - 0.175{*}10^5T^{-2} + 28621T^{-1} - 470.02.$$

$SmCl_3$ liquid, 950 K < T < 1300 K:

$$C^0_{p,m} = 145.26,$$
$$H^0_m(T) - H^0_m(298.15) = 145.26{*}10^{-3}T - 19.16,$$
$$S^0_m(T) = 145.26 \ln T - 671.02,$$
$$-(G^0_m(T) - H^0_m(298.15))/T = 145.26 \ln T + 19160\, T^{-1} - 816.46.$$

Having the thermodynamic functions for $SmCl_3$, one can calculate the thermodynamic functions of its formation as a function of temperature.

The formation of $SmCl_3$ from the elements can be described by the reaction

$$Sm(s) + 1.5\ Cl_2(g) = SmCl_3(s,l), \quad (2)$$

and the related thermodynamic functions of $SmCl_3$ formation depend on the thermodynamic functions of metallic Sm and chlorine gas Cl_2. The latter were calculated using literature data for $C^0_{p,m}$ and $S^0_m(298.15\ K)$ [9]. The enthalpy of $SmCl_3$ formation at 298.15 K, $\Delta_{form}H^0_m(SmCl_3, s, 298.15\ K)$ = –1025.3 kJ mol^{-1}, also required in this calculation, was taken from Cordfunke and Konings recent work [14].

Two phase changes occur in this system described by reaction (2): the first one is the melting of $SmCl_3$ at 950 K, and the second one the $\alpha \rightarrow \beta$ solid-solid phase transition of Sm at 1190 K with the enthalpy of 3.1 kJ mol^{-1} [9]. Accordingly, the formation enthalpy $\Delta_{form}H^0_m$ (kJ mol^{-1}) and the Gibbs energy of formation $\Delta_{form}G^0_m$ (kJ mol^{-1}) are described by the equations given below:

$SmCl_3$ solid, 298.15 K < T < 950 K:

$$\Delta_{form}H^0_m = 8.366{*}10^{-3}T - 0.444{*}10^{-6}T^2 - 9.527{*}10^2T^{-1} + 3.487{*}10^{-9}T^3 - 1024.6,$$
$$\Delta_{form}G^0_m = 304.636{*}10^{-3}T + 0.444{*}10^{-6}T^2 - 4.763{*}10^2T^{-1} - 1.743{*}10^{-9}T^3 - 8.344{*}10^{-3}T \ln T - 1024.6.$$

$SmCl_3$ liquid, 950 K < T < 1190 K:

$$\Delta_{form}H^0_m = 62.366{*}10^{-3}T - 14.978{*}10^{-6}T^2 - 9.878{*}10^2T^{-1} + 3.487{*}10^{-9}T^3 - 1015.2,$$
$$\Delta_{form}G^0_m = 651.101{*}10^{-3}T + 14.978{*}10^{-6}T^2 - 4.939{*}10^2T^{-1} - 1.743{*}10^{-9}T^3 - 62.366{*}10^{-3}T \ln T - 1015.0.$$

$SmCl_3$ liquid, 1190 K < T < 1300 K:

$$\Delta_{form}H^0_m = 42.966{*}10^{-3}T - 0.188{*}10^{-6}T^2 - 4.268{*}10^2T^{-1} - 1010.7,$$
$$\Delta_{form}G^0_m = 524.911{*}10^{-3}T + 0.188{*}10^{-6}T^2 - 2.134{*}10^2T^{-1} - 42.966{*}10^{-3}T \ln T - 1009.6.$$

The results obtained for selected temperatures are presented in Table 2.

$TmCl_3$

The only existing literature data on the $TmCl_3$ heat capacity are the experimental data at low temperatures (10 - 300 K) obtained by Tolmach et al. [15] by adiabatic calorimetry (100.10 J K^{-1}mol^{-1} at 300 K). Barin and Knacke [12] as well as Knacke et al. [11] made heat capacity estimations. Our experimental heat capacity values on $TmCl_3$, are presented in Figure 2. They agree very well with these estimations as with the low temperature experimental data. Unfortunately we could not do measurements for liquid $TmCl_3$ because of limitations of the apparatus.

Our experimental heat capacity data were fitted to the polynomial (1) with the contraint that $C^0_{p,m}(TmCl_3, s, 298.15\ K)$ be equal to the reported literature value 100.00 J K^{-1}mol^{-1} [15].

The thermodynamic functions of thulium trichloride were calculated up to 1300 K using our experimental melting temperature and enthalpy to-

Fig. 2. Molar heat capacity of $TmCl_3$. Open circles: experimental values, black circle: low temperature datum [15], solid line: polynomial fitting of experimental values.

Table 3. The calculated thermodynamic functions of $TmCl_3$ at selected temperatures from 298.15 to 1300 K.

T	$C_{p,m}$	S^0_m	$-(G-H_{298.15})/T$	H_T-H_{298}	$\Delta_{form}H^0_m$	$\Delta_{form}G^0_m$
K	— J K^{-1}mol^{-1} —			— kJ mol^{-1} —		
298.15	100.00	150.60	150.60	0.00	–996.3	–919.4
300	100.02	151.22	150.60	0.18	–996.3	–918.9
400	101.10	180.14	154.54	10.24	–994.1	–893.5
500	102.16	202.82	162.01	20.40	–991.9	–868.6
600	103.20	221.53	170.41	30.67	–989.8	–844.1
700	104.23	237.52	178.88	41.04	–987.8	–820.0
800	105.26	251.51	187.11	51.52	–985.7	–796.2
900	106.29	263.96	194.97	62.10	–983.6	–772.6
1000	107.32	275.22	202.44	72.78	–981.5	–749.3
1092	108.27	284.70	208.97	82.69	–979.6	–728.0
1092	148.53	317.30	208.97	118.29	–944.0	–728.0
1100	148.53	318.39	209.76	119.48	–943.5	–726.4
1200	148.53	331.31	219.36	134.34	–937.5	–707.0
1300	148.53	343.20	228.43	149.19	–931.5	–688.0

gether with heat capacity data. The standard entropy $S^0_m(TmCl_3, s, 298.15\ K) = 150.60$ J K^{-1}mol^{-1} was taken from [16]. Additionally we used the heat capacity value in [9] of liquid $TmCl_3$, $C^0_{p,m}(TmCl_3, l) = 148.53$ J K^{-1}mol^{-1}.

Our polynomial dependence of the heat capacity on temperature was thus used to calculate the heat capacity $C^0_{p,m}(T)$ in J K^{-1}mol^{-1}, enthalpy increments $H^0_m(T) - H^0_m(298.15\ K)$ in kJ mol^{-1}, entropy S^0_m and Gibbs energy functions $(G^0_m(T) - H^0_m(298.15))/T$ in J K^{-1}mol^{-1}, both for solid and liquid $TmCl_3$. The corresponding equations are given below. The results for selected temperatures are presented in Table 3.

$TmCl_3$ solid, 298.15 K < T < 1092 K:

$$C^0_{p,m} = 97.08 + 10.254{*}10^{-3}T - 0.12{*}10^{5}T^{-2},$$

$$H^0_m(T) - H^0_m(298.15) = 97.08{*}10^{-3}T + 5.127{*}10^{-6}T^2, + 0.12{*}10^{2}T^{-1} - 29.44,$$

$$S^0_m(T) = 97.08 \ln T + 10.254{*}10^{-3}T + 0.06{*}10^{5}T^{-2} - 405.64,$$

$$-(G^0_m(T) - H^0_m(298.15))/T = 97.08 \ln T + 5.127{*}10^{-3}T - 0.06{*}10^{5}T^{-2} + 29440T^{-1} - 502.71.$$

$TmCl_3$ liquid, 1092 K < T < 1300 K:

$$C^0_{p,m} = 148.53,$$

$$H^0_m(T) - H^0_m(298.15) = 148.53{*}10^{-3}T - 43.90,$$

$$S^0_m(T) = 148.53 \ln T - 721.79,$$

$$-(G^0_m(T) - H^0_m(298.15))/T = 148.53 \ln T + 43903T^{-1} - 870.33.$$

As done for $SmCl_3$, the thermodynamic functions of $TmCl_3$ formation were calculated.

This formation from the elements can be described by the reaction

$$Tm(s) + 1.5\ Cl_2(g) = TmCl_3(s,l). \quad (3)$$

The thermodynamic functions of metallic Tm and gaseous Cl_2, $C^0_{p,m}$ and $S^0_m(298.15\ K)$, necessary for the calculation, were taken from [9]. The enthalpy of $TmCl_3$ formation, $\Delta_{form}H^0_m(TmCl_3, s, 298.15\ K) = -935.4$ kJ mol^{-1}, also required, was taken from Cordfunke and Konings [14].

Only one phase change occurs in this system described by reaction (3): it is the melting of $TmCl_3$ at 1092 K. Accordingly, the formation enthalpy $\Delta_{form}H^0_m$ (kJ mol^{-1}) and Gibbs energy of formation $\Delta_{form}G^0_m$ (kJ mol^{-1}) are described by the equations

$TmCl_3$ solid, 298.15 K < T < 1092 K:

$$\Delta_{form}H^0_m = 21.894{*}10^{-3}T - 1.566{*}10^{-6}T^2 - 0.928{*}10^{2}T^{-1} + 0.627{*}10^{-9}T^3 - 1002.4,$$

$$\Delta_{form}G^0_m = 403.179{*}10^{-3}T + 1.566{*}10^{-6}T^2 - 0.464{*}10^{2}T^{-1} - 0.363{*}10^{-9}T^3 - 21.894{*}10^{-3}T \ln T - 1002.4.$$

$TmCl_3$ liquid, 1092 K < T < 1300 K:

$$\Delta_{form}H^0_m = 73.348{*}10^{-3}T - 6.693{*}10^{-6}T^2 - 1.048{*}10^{2}T^{-1} + 0.627{*}10^{-9}T^3 - 1016.9,$$

$$\Delta_{form}G^0_m = 770.791{*}10^{-3}T + 6.693{*}10^{-6}T^2 - 0.524{*}10^{2}T^{-1} - 0.363{*}10^{-9}T^3 - 73.348{*}10^{-3}T \ln T - 1016.9.$$

In 1971 Dworkin and Bredig [17] have made a correlation between the crystal structure of lanthanide chlorides and their entropy of melting. They have found that for lanthanide chlorides with the $Y(OH)_3$-type structure ($LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, and $GdCl_3$) the entropy of melting $\Delta_{fus}S^0_m(LnCl_3, T_m)$ is about (50±4) J K^{-1}mol^{-1}, whereas for the lanthanide chlorides with the $AlCl_3$-type structure ($DyCl_3$, $ErCl_3$) this entropy or the sum of the entropies of transition and of fusion $\Delta_{trs}S^0_m(LnCl_3, s, T_{trs}) + \Delta_{fus}S^0_m(LnCl_3, T_{fus})$ is significantly lower and equal to (31±4) J K^{-1}mol^{-1}.

Tosi et al. [18] have developed these observations and have proposed that the melting mechanism of trivalent metal chlorides can be classified into three main types in correlation with the character of the

chemical bond. They have classified the lanthanide chlorides into three groups depending on the crystal structure: $AlCl_3$-, UCl_3-, and $PuBr_3$-type structure. The $AlCl_3$-type structure is layered and can almost be viewed as cubic close packing of Cl ions inside which the metal ions occupy suitable octahedral sites. The UCl_3-type structure (also known as the $Y(OH)_3$-type structure) is described as hexagonal, with each U surrounded by six Cl on the corner of a trigonal prism and further coordinated by the three coplanar Cl's at somewhat larger distance. The $PuBr_3$-type structure appears to be of a transitional type between the $AlCl_3$- and UCl_3-type structures.

In summary, the melting from the UCl_3-type ($LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$ and $GdCl_3$) or $PuBr_3$-type structure ($TbCl_3$) involves appreciably higher entropies than from the $AlCl_3$-type ($ErCl_3$, $HoCl_3$, $DyCl_3$). The values of this entropies are (50±4), (40.9) and (31±4) J $K^{-1}mol^{-1}$, respectively.

We have determined previously the sum $\Delta_{trs}S^0_m + \Delta_{fus}S^0_m$ for $TbCl_3$ ($PuBr_3$-type structure) [19] and $ErCl_3$ ($AlCl_3$- type structure) [1], that is in excellent agreement with the above observations (41.9 and 34.9 J $K^{-1}mol^{-1}$, respectively). Moreover, looking at the values of the melting entropy $\Delta_{fus}S^0_m(SmCl_3, T_{fus})$ = 50.3 J $K^{-1}mol^{-1}$ and $\Delta_{fus}S^0_m(EuCl_3, T_{fus})$ = 50.3 J $K^{-1}mol^{-1}$ [3], one can come to the conclusion that these chlorides both have the UCl_3-type structure, whereas $TmCl_3$($\Delta_{fus}S^0_m(TmCl_3, T_{fus})$ = 32.6 J $K^{-1}mol^{-1}$) has the $AlCl_3$-type structure. This is in excellent agreement with literature data: $SmCl_3$ and $EuCl_3$ have the UCl_3-type structure [7] and $TmCl_3$ the $AlCl_3$-type structure [20].

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