*Thermochimica Acta*, 133 (1988) 275–282
Elsevier Science Publishers B.V., Amsterdam

# PROPERTIES OF DOUBLE CHLORIDES IN THE SYSTEMS $ACl/SmCl_3$ (A=Na-Cs)

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## ABSTRACT

The phase diagrams of the systems $ACl/SmCl_3$(A=Na-Cs) were reinvestigated by DTA; the thermodynamic stabilities of the existing double chlorides were determined by solution calorimetry and e.m.f.-measurements in galvanic cells with solid electrolytes. Furthermore, their magnetic susceptibilities and crystal structures were measured.

## INTRODUCTION

In continuation of our research work about the properties of ternary chlorides in systems $ACl/LnCl_3$(Ln=La[1], Ce[2], Pr[3], Nd[4]) we now have investigated the systems of alkalimetal chlorides ACl with $SmCl_3$ . Of special interest in this context was the question if the smaller ionic radius of $Sm^{3+}$ (0.96 pm) compared with Nd (1.00 pm) would already cause a variation in the coordination of the lanthanide ion.

## EXPERIMENTAL

Preparation of compounds: $SmCl_3$= dehydration of the hydrate in an HCl-stream. - $SmCl_3 \cdot 6H_2O$: crystallized from a solution of $Sm_2O_3$ (Fa. Ventron, 99.999%) in hydrochloric acid. - Alkalimetal chlorides: p.A.-quality, Fa. Merck; dried at 500°C in HCl.
Ternary chlorides: prepared by fusion in vacuum sealed quartz ampoules; if necessary annealed. All manipulations in a glove-box (10 ppm $H_2O$).
DTA-measurements: heating curves (2 deg· $min^{-1}$). Preparation of the samples like the ternary chlorides.
Solution calorimetry: Home-built isoperibolic calorimeter. From the enthalpies of solution, $\Delta H^l$, the reaction enthalpies, $\Delta H^f$, were calculated:

$$\Delta H^f_{298} = (\Delta H^l_{298}(SmCl_3)+n\Delta H^l_{298}(ACl)) - \Delta H^l_{298}(A_nSmCl_{n+3})$$

*Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988*
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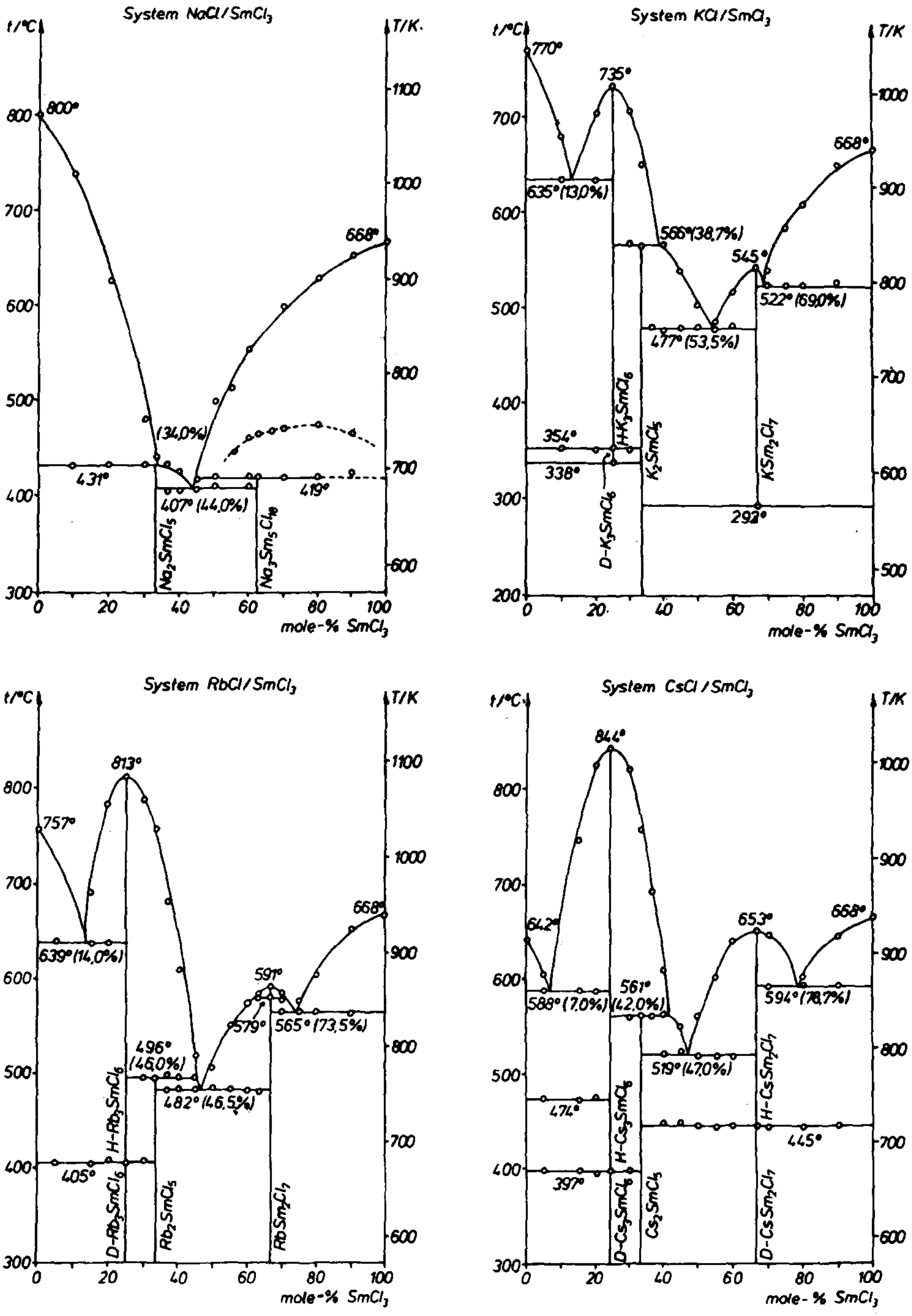

Fig. 1 Phase diagrams of the systems $ACl/SmCl_3$

X-ray-powder patterns: Philips PW 1050/25 goniometer. - High-temperature photos: Simon-Guinier method (Standard: $Al_2O_3$ with a=475.9 pm; c=1299.0 pm).
Magnetic measurements: Gouy method at several temperatures in the range from -200 to 100°C. Calibration with $HgCo(SCN)_4$: $\chi_g = 16.515 \cdot 10^{-6} cm^3 \cdot g^{-1}$ at 18.5°C. E.m.f.-measurements: A description of the galvanic cell is given elsewhere [5]. For the formation of the $SmCl_3$-richest compound the set-up of the cell was

$$(C+Cl_2)/ACl/A^+\text{-conducting diaphragm}/SmCl_3(+A_nSmCl_{n+3})/(C+Cl_2).$$

The solid electrolytes (compressed disks) were separated by a sintered disk of an $A^+$-conducting glass powder, available for A=Na,K,Rb. The collected e.m.f./T values were subjected to a linear regression analysis. Temperature range: 300-480°C.

## THE PHASE DIAGRAMS

Fig. 1 illustrates the results of the DTA-measurements. The melting point of $SmCl_3$ was found in good agreement with literature [6] at 668°C. - In general the older findings of Korshunov et al. [7] could be confirmed, however with the following additions:

$NaCl$-$SmCl_3$: An additional compound exists, $Na_3Sm_5Cl_{18}$. Like the analogous phases in the systems with La-Nd, there is a mixed-crystal region at higher temperature; the exact boundaries could not be fixed.

$KCl$-$SmCl_3$ [8]: The compounds $K_3SmCl_3$ (with an polymorphic transformation at 354°C) and $KSm_2Cl_7$ are stable only at temperatures higher than 338°C and 292°C resp.. $K_3SmCl_6$ is the only ternary chloride of $Sm^{3+}$ which could not be obtained by quenching without decomposition.

$CsCl$-$SmCl_3$: An addtional compound. $Cs_2SmCl_5$, is existing with an incongruently melting point at 561°C.

## CRYSTAL STRUCTURES AND MAGNETIC MOMENTS

The structures of most of the compounds $A_2SmCl_5$ and $ASm_2Cl_7$ were already known by the work of Meyer: $Rb_2SmCl_5$, $K_2SmCl_5$=$K_2PrCl_5$-type [9]; $CsSm_2Cl_7$, $RbSm_2Cl_7$= $RbDy_2Cl_7$-type and $KSm_2Cl_7$=$KDy_2Cl_7$-type [10].
The hitherto unknown structural dates are compiled in tab. 1. $Cs_2SmCl_5$ is crystallizing with the $Cs_2DyCl_5$-structure [11]. The structures of the low-temperature modifications of $Rb_3SmCl_6$ and $K_3SmCl_6$ could not be solved from powder patterns. $Na_3Sm_5Cl_{18}$ is isotypic to $K_3La_5Cl_{18}$ (≡ $KLa_{1.67}Cl_6$) [1].

**Table 1 Unit cell parameters for samarium double chlorides**

| Compound | Space group | a/pm | b/pm | c/pm | β/grad |
|---|---|---|---|---|---|
| H-$Cs_3SmCl_6$ | Fm3m | 1162.0 | | | |
| D-$Cs_3SmCl_6$ | $P2_1/c$ | 1402.0 | 820.7 | 1320.6 | 107.70 |
| H-$Rb_3SmCl_6$ | Fm3m | 1127.8 | | | |
| H-$K_3SmCl_6$ | Fm3m | 1107.8 | | | |
| $Cs_2SmCl_5$ | Pnma | 962.4 | 758.0 | 1528.6 | |
| $Na_2SmCl_5$ | Pnma | 1204.8 | 835.9 | 769.2 | |
| $Na_3Sm_5Cl_{18}$ | $P6_3/m$ | 751.9 | | 416.1 | |
| $SmCl_3$ | $P6_3/m$ | 738.8 | | 417.6 | |
| $SmCl_3$[12] | $P6_3/m$ | 737.8 | | 417.1 | |

For $Sm^{3+}$ ($4f^5$-electrons in $^6H_{5/2} \longrightarrow g = 2/7$) the magnetic moment $\mu_{eff} = g\cdot\sqrt{J(J+1)}\cdot\mu_B$ should be $0.84\mu_B$. However, it is well known that moments of ~$1.5\mu_B$ at room temperature are found: caused by a small spin-orbit coupling the term-splitting is of the magnitude k·T; a temperature - independent paramagnetism must be added (2. order Zeeman-effect). Thus, the moments are temperature dependet; for $SmCl_3$ [13] they increase in the range from 80 to 289 K from 1.04 to $1.56\mu_B$. The same behaviour was found for the ternary chlorides (tab. 2).

**Table 2 Magnetic moments [$\mu_B$] in dependence on temperature**

| Compound | 78K | 130K | 198K | 293K | 366K |
|---|---|---|---|---|---|
| $SmCl_3$ | 1.06 | 1.22 | 1.39 | 1.62 | 1.79 |
| $CsSm_2Cl_7$ | 0.96 | 1.18 | 1.37 | 1.60 | 1.75 |
| $Cs_2SmCl_5$ | 0.92 | 1.15 | 1.36 | 1.60 | 1.77 |
| $Cs_3SmCl_6$ | 0.89 | 1.13 | 1.33 | 1.61 | 1.75 |
| $RbSm_2Cl_7$ | 0.99 | 1.20 | 1.38 | 1.61 | 1.77 |
| $Rb_2SmCl_5$ | 0.93 | 1.13 | 1.33 | 1.55 | 1.73 |
| $Rb_3SmCl_6$ | 0.89 | 1.08 | 1.32 | 1.59 | 1.74 |
| $KSm_2Cl_7$ | 1.01 | 1.20 | 1.38 | 1.62 | 1.79 |
| $K_2SmCl_5$ | 0.98 | 1.18 | 1.38 | 1.59 | 1.76 |
| $Na_3Sm_5Cl_{18}$ | 1.04 | 1.22 | 1.39 | 1.62 | 1.80 |
| $Na_2SmCl_5$ | 1.00 | 1.19 | 1.38 | 1.60 | 1.77 |

## SOLUTION CALORIMETRY AND E.M.F. MEASUREMENTS

The solution enthalpies for the ternary chlorides at 298 K ($\Delta H^{l}_{298}$), the formation enthalpies from ACl and $SmCl_3$ ($\Delta H^{f}_{298}$) and enthalpies of synproportionation ($\Delta H^{s}_{298}$) are compiled in table 3. $\Delta H^{l}_{298}$ ($SmCl_3$) was found to be -164.7± 0.2kJ· mol$^{-1}$ (Literature: -163.2 to 167.1 kJ· mol$^{-1}$ [14]. The enthalpies for dissolving the alkali metal chlorides in $SmCl_3$-solutions are (kJ· mol$^{-1}$): CsCl= 18.1; RbCl= 17.6; KCl= 17.9; NaCl= 4.5. As 'neighbour-compounds' for the synproportionations those were elected, which are itselves stable at or near 298 K.

The e.m.f.-values were measured for the formation of each compound from ACl(A= Rb,K,Na) and the adjacent $SmCl_3$-richer compound. The regression line for the e.m.f./ T-values was transformed by multiplication with -n·F to the Gibbs-Helmholtz equation $\Delta G^{r} = \Delta H^{r} - T\cdot \Delta S^{r}$. By means of thermodynamic cycles,these functions were transformed to those for the reactions $nACl + SmCl_3 = A_nSmCl_{n+3}$, denoted $\Delta G^{f}$, $\Delta H^{f}$, $\Delta S^{f}$, and further to the free enthalpies of synproportionation, $\Delta G^{s}$, from the two neighboured compounds. For high-temperature modifications the temperatures of formation (decomposition) were calculated by the condition $\Delta G^{s} = 0 \longrightarrow \Delta H^{s} = T\cdot\Delta S^{s}$.

**Table 3 Solution enthalpies $\Delta H^{l}$ and related enthalpy values in kJ· mol$^{-1}$**

| Compound | $\Delta H^{l}_{298}$ | $\Delta H^{f}_{298}$ | $\Delta H^{s}_{298}$ | synprop. from | Literature [14] |
|---|---|---|---|---|---|
| ½ $CsSm_2Cl_7$ | -137.8 | -17.9 | - 9.2 | $Cs_2SmCl_5$,$SmCl_3$ | $\Delta H^{l}$:-127.25 $\Delta H^{f}$=-28.7 |
| $Cs_2SmCl_5$ | - 93.7 | -34.8 | + 6.2 | $Cs_3SmCl_6$,$CsSm_2Cl_7$ | |
| $Cs_3SmCl_6$ | - 54.1 | -56.3 | -24.4 | CsCl, $Cs_2SmCl_5$ | $\Delta H^{l}$:- 53.9 $\Delta H^{f}$=-58.6 |
| ½ $RbSm_2Cl_7$ | -141.1 | -14.8 | - 1.6 | $Rb_2SmCl_5$,$SmCl_3$ | |
| $Rb_2SmCl_5$ | - 73.3 | -55.8 | -43.9 | RbCl, $RbSm_2Cl_7$ | |
| $Rb_3SmCl_6$ | - 71.6 | -40.3 | +12.6 | RbCl, $Rb_2NdCl_5$ | |
| ½ $KSm_2Cl_7$ | -153.7 | - 2.2 | + 8.1 | $K_2SmCl_5$, $SmCl_3$ | $\Delta H^{l}$:-155.05 $\Delta H^{f}$:- 0.9 |
| $K_2SmCl_5$ | - 87.7 | - 41.2 | - 41.2 | KCl, $SmCl_3$ | |
| $K_3SmCl_6$ | - | - | - | - | $\Delta H^{l}$:-112.5 $\Delta H^{f}$:-16.9 |
| ⅕ $Na_3Sm_5Cl_{18}$ | -166.7 | + 4.7 | - | - | |
| $Na_2SmCl_5$ | -170.1 | +14.4 | - | - | |

### Results of Measurements

$0.5 RbCl + SmCl_3 = Rb_{0.5}SmCl_{3.5}$ . For this reaction the time to approach equilibrium was very long (some days). Therefore only one value was measured; the entropy was calculated by using the $\Delta H^{f}$-value from solution calorimetry (-14.8kJ· mol$^{-1}$).

Measured e.m.f. at 673K: 340mV. $\Delta G^r = \Delta G^f/\mathrm{kJ\cdot mol^{-1}} = 14.8-0.0024\cdot T$

1.5 $RbCl+Rb_{0.5}SmCl_{3.5} = Rb_2SmCl_5$ $\Delta G^r/\mathrm{kJ\cdot mol^{-1}} = -40.7+0.0090\cdot T/K$
for $2RbCl+SmCl_3 = Rb_2SmCl_5$ $\Delta G^f/\mathrm{kJ\cdot mol^{-1}} = -55.5+0.0066\cdot T/K$

$RbCl+Rb_2SmCl_5 =$ H-$Rb_3SmCl_6$ $\Delta G^r/\mathrm{kJ\cdot mol^{-1}} = 22.7-0.0581\cdot T/K$
$RbCl+Rb_2SmCl_5 =$ D-$Rb_3SmCl_6$ $\Delta G^r/\mathrm{kJ\cdot mol^{-1}} = 14.5-0.0459\cdot T/K$
Transformation Temperature D ⟶ H (fig. 2): $\Delta G^r(H) = \Delta G^r(D)$ at 673 K (400°C)
Enthalpy of transformation = 8.2 kJ·mol$^{-1}$; entropy of transformation = 12.2 J·K$^{-1}$·mol$^{-1}$

0.5 $KCl+SmCl_3 = K_{0.5}SmCl_{3.5}$ $\Delta G^r \equiv \Delta G^f/\mathrm{kJ\cdot mol^{-1}} = 0.3-0.0210\cdot T/K$

1.5 $KCl+K_{0.5}SmCl_{3.5} = K_2SmCl_5$ $\Delta G^r/\mathrm{kJ\cdot mol^{-1}} = -41.5+0.0105\cdot T/K$
for $2KCl+SmCl_3 = K_2SmCl_5$ $\Delta G^f/\mathrm{kJ\cdot mol^{-1}} = -41.5-0.0105\cdot T/K$

$KCl+K_2SmCl_5 =$ H-$K_3SmCl_6$ $\Delta G^r/\mathrm{kJ\cdot mol^{-1}} = 38.6-0.0634\cdot T/K$
$KCl+K_2SmCl_5 =$ D-$K_3SmCl_6$ $\Delta G^r/\mathrm{kJ\cdot mol^{-1}} = 30.4-0.0502\cdot T/K$
Transformation temperature D ⟶ H: $\Delta G^r(H) = \Delta G^r(D)$ at 615K (342°C)
Enthalpiy of transformation = 8.2kJ·mol$^{-1}$; entropy of transformation = 13.2 J·K$^{-1}$·mol$^{-1}$

0.6 $NaCl+SmCl_3 = Na_{0.6}SmCl_{3.6}$ $\Delta G^r \equiv \Delta G^f/\mathrm{kJ\cdot mol^{-1}} = 6.1-0.0149\cdot T/K$

1.4 $NaCl+Na_{0.6}SmCl_{3.6} = Na_2SmCl_5$ $\Delta G^r = 9.8-0.0233\cdot T/K$
for $2NaCl+SmCl_3 = Na_2SmCl_5$ $\Delta G^f = 16.0-0.0382\cdot T/K$

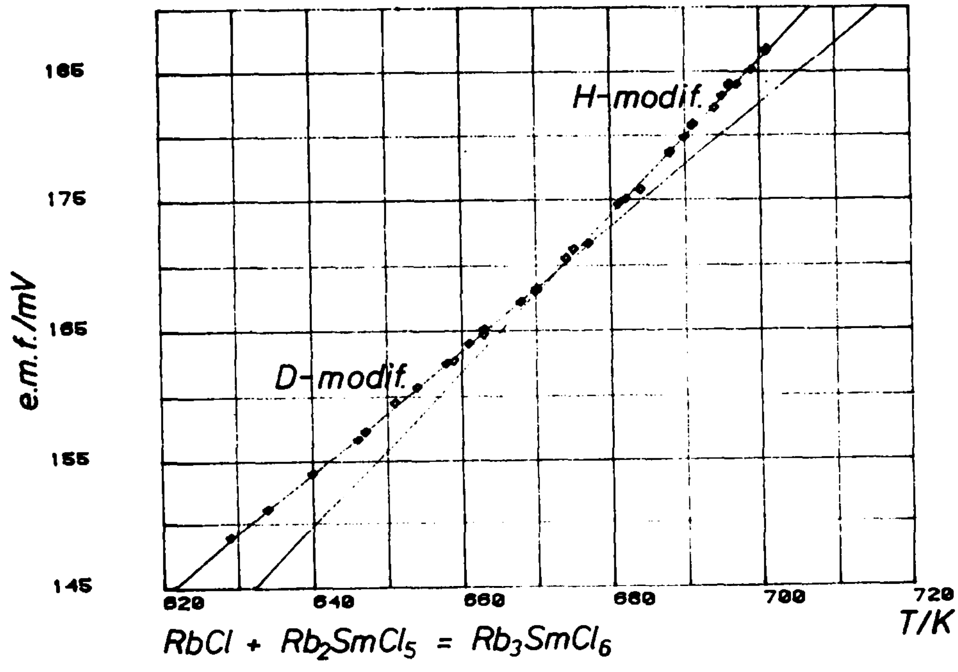

Fig. 2 EMF vs. T values for the reaction $RbCl+Rb_2SmCl_5 = Rb_3SmCl_6$

In tab. 4 the values for the thermodynamic functions at T= 298 K are compiled as terms of the Gibbs-Helmholtz equation together with the $\Delta G^s$-values for this temperature.

**Table 4 Energies of the formation from ACl and $SmCl_3$ at 298K and free enthalpies of synproportionation $\Delta G^s_{298}$ (in kJ· mol$^{-1}$ )**

| Compound | $\Delta G^f$ | $\Delta H^f$ | $-(T\cdot\Delta S^f)$ | $\Delta H^f_{cal.}$ | $\Delta G^s$ | $\Delta G^s=0$ at T/K |
|---|---|---|---|---|---|---|
| $Rb_{0.5}SmCl_{3.5}$ | -15.5 | (-14.8) | - 0.7 | -14.8 | -11 | |
| $Rb_2SmCl_5$ | -53.5 | -55.5 | + 2.0 | -55.8 | -38.0 | |
| H-$Rb_3SmCl_6$ | -49.7 | -32.8 | -16.9 | - | + 5.9 | |
| D-$Rb_3SmCl_6$ | -52.7 | -41.0 | -11.7 | -40.3 | + 0.9 | 317 (44°C) |
| $K_{0.5}SmCl_{3.5}$ | - 6.6 | - 0.3 | - 6.3 | - 2.2 | + 4.7 | |
| $K_2SmCl_5$ | -44.9 | -41.8 | - 3.1 | -41.2 | -41.9 | |
| H-$K_3SmCl_6$ | -25.2 | - 3.2 | -22.0 | - | +19.7 | |
| D-$K_3SmCl_6$ | -29.3 | -11.2 | -18.1 | - | +15.4 | 605 (323°C) |
| $Na_{0.6}SmCl_{3.6}$ | + 1.7 | + 6.1 | - 4.4 | + 4.7 | + 0.1 | 354 (81°C) |
| $Na_2SmCl_5$ | + 4.6 | +16.0 | - 11.4 | +14.4 | + 2.9 | 423 (150°C) |

## CONCLUSIONS

1) In the system $NaCl/SmCl_3$ a phase $Na_3Sm_5Cl_{18}$ exists at temperatures >81°C. Like the analogous phases in the other systems La-Nd it can be considered as a solid solution of NaCl in the $LnCl_3$-lattice. Additionally, a compound $Na_2SmCl_5$ is existing at t > 150°C, crystallizing with the $K_2SrCl_5$-structure.

2) In the systems of $SmCl_3$ with KCl, RbCl, CsCl there exist three compounds like in all other systems from La-Nd, $A_3LnCl_6$, $A_2LnCl_5$, $ALn_2Cl_7$. $K_2SmCl_5$ and $Rb_2SmCl_5$ are crystallizing with the $K_2PrCl_5$-structure as compounds $A_2LnCl_5$ with the earlier lanthanides. As the $\Delta G^s$-values in table 4 show, these compounds are stable at room temperature. $Cs_2SmCl_5$ is the first 2:1-compound in this series with the $Cs_2DyCl_5$-structure: the $Sm^{3+}$ is located in a $Cl_6$-octahedron and not in a single-capped prism as in the $K_2PrCl_5$-type. The coordination number has decreased from 7 to 6! According to the $\Delta H^s$-values in table 3, there is a small loss in lattice energy by the formation from the adjacent compounds. In this system $Cs_3SmCl_6$ has the greatest $\Delta H^s$-value. As all other compounds $A_3SmCl_6$, the high-temperature form has the elpasolite structure (C.N.=6), the D-modification crystallizes in the monoclinic $K_3MoCl_6$-type [15]. The compounds $ASm_2Cl_7$ with A=K,Cs are unstable

at ambient temperature. They have no longer the β-$KEr_2F_7$ structure but are crystallizing in the $RbDy_2Cl_7$- and $KDy_2Cl_7$-type resp.; the coordination number remains seven.

3) As the T· ΔS-term in table 4 demonstrates, all compounds unstable at ambient temperature are existing from a gain in entropy.

This work was supported by the Deutsche Forschungsgemeinschaft and the Fond der Chemischen Industrie.

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