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Review Paper

TERNARY CHLORIDES OF THE TRIVALENT EARLY LANTHANIDES

Phase diagrams, crystal structures and thermodynamic properties

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Abstract

A comprehensive review on phase diagrams, crystal structures and thermodynamics of ternary chlorides formed in systems ACl/$LnCl_3$ (*A*=Cs, Rb, K, Na; *Ln*=La–Gd) is presented. The review summarizes the author's own studies, published since 1985, and original papers of other scientists. With the larger alkali metal ions compounds such as A_3LnCl_6, A_2LnCl_5 and ALn_2Cl_7 were obtained. With sodium additional compounds $NaLnCl_4$ and $Na_3Ln_5Cl_{18}$ were obtained. The crystal structures are discussed with the concept of ionic radii, which determine the coordination numbers of Ln^{3+} and A^+ cations against Cl^- anions. The formation enthalpies of the compounds from ACl and $LnCl_3$ were determined by solution calorimetry. Gibbs' free energies and entropies for these reactions were obtained by e.m.f. measurements *vs.* temperature.

The stability of a ternary chloride in a system ACl–$LnCl_3$ is given by the 'free enthalpy of synproportionation', that is, the formation of a compound from its neighbour compounds in the system. This ΔG^0_{syn} must be negative. A surprising result is, that the highest-melting compounds in the systems, A_3LnCl_6, are formed from ACl+A_2LnCl_5 by a loss in lattice energy. They exist as high-temperature compounds due to sufficiently high gain in entropy at temperatures where $T\Delta S>\Delta H$.

Keywords: alkali metal ions, crystal structures, lanthanide ions, phase diagrams, thermodynamic data, ternary chlorides

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Introduction

For systematic solid-state chemistry the group of lanthanides (*Ln*) – lanthanum (La) and the 14 elements from Ce to Lu – offers two advances: all elements form stable compounds of oxidation state three, and the radii of these trivalent ions decrease more or less continuously. It is a similar situation as with the light transition elements, where we find a separate group of 10 elements with divalent ions from Sc to Zn. The existence of double chlorides with alkali metal chlorides, ACl, where A is an alkali metal cation, is well investigated. The predominating compounds with the composition $AMCl_3$, where M is the transition element divalent cation, crystallize with the perovskite structure or its variants. Not so comprehensive are the investigations on ternary lanthanide chlorides. Russian scientists elucidated the phase diagrams of most of the pseudobinary systems $ACl/LnCl_3$ by means of DTA. Systematic X-ray structure determinations were performed with some groups of compounds by Meyer in Germany. However, for a long period nearly nothing was known about the thermodynamic stability of these compounds, with the exception of calorimetric measurements by Blachnik and co-workers in the seventies. In the last two decades systematic papers about the thermodynamic of $ACl–LnCl_3$-melts, also containing results of calorimetric measurements on solid double chlorides, were published by Gaune-Escard [69–71] in Marseille together with scientists from Wroclaw.

This situation was the starting point of our own investigations in 1984. We elucidated the phase diagrams by means of DTA and X-ray analysis with crystal powders. In special cases we also used high-temperature X-ray photography to determine the kind of solid-state reactions that were found with DTA. The DTA-peak alone only tells us that a reaction has occurred, but it cannot distinguish between polymorphic structure changes, decomposition or formation reactions.

Besides X-ray-diffraction the best method to identify the nature of a solid-state reaction is by the determination of Gibbs' free energy curves as a function of the temperature with a galvanic cell for solid electrolytes, using the relation $\Delta Gz–nFE$, where E is the e.m.f. of the cell, n is the transported charge and F is the Faraday constant. We developed such cells for chloride systems at the end of the seventies [1].

Let us assume that in a system KCl/MCl_3 a ternary compound $KMCl_4$ exists at temperatures above T_f (where T_f is the formation temperature). Then we can build a cell in which the reaction $KCl(S)+MCl_3(S)=KMCl_4(S)$ (where S denotes solid) will produce an e.m.f. with a negative ΔG. The set up of the cell is $(C+Cl_2)/KCl/K^+$-conducting diaphragm/MCl_3 $(+AMCl_4)/(C+Cl_2)$. More details about these cells can be found in [1].

In all hitherto conducted measurements the dependency of ΔG on temperature (T) has proven to be linear. This allows the calculation of the other two functions, ΔH and ΔS, using the Gibbs–Helmholtz-equation $\Delta G=\Delta H–T\Delta S$. Additionally, ΔH at T=298 K can be measured by solution-calorimetry. The results of these thermodynamic measurements are given in the second part of this paper.

At temperatures higher than T_f the formation reaction of $KMCl_4$ is accompanied by negative ΔG values. At temperatures lower than T_f, the compound is not stable any more and ΔG becomes zero. That is, at all temperatures, where a compound does not exist, the e.m.f. is zero. Therefore, we have an excellent probe for detecting the existence of double chlorides in systems of interest. Together with the X-ray analysis, especially when we succeed in indexing the powder patterns according to a known structure type or by solving the structure with single crystal techniques, we may have correct data about the stoichiometry and the regions of existence of a double chloride.

Since 1985 we have done this study for the light lanthanides from La to Gd. The results for the particular systems are given in papers, compiled in Table 1. Systems with LiCl are excluded. Because of the aggressivity of LiCl melts we could not perform measurements with our special equipment.

Table 1 Ternary lanthanide chloride systems investigated in Kassel

Year	System	Reference
1985	$ACl/LaCl_3$	[1]
1986	$ACl/CeCl_3$	[2]
1987	$ACl/PrCl_3$	[3]
1988	$ACl/NdCl_3$	[4]
1988	$ACl/SmCl_3$	[5]
1990	$ACl/EuCl_3$	[6]
1990	$ACl/GdCl_3$	[7]

Phase diagrams of systems $ACl/LnCl_3$ and the crystal structures of the existing ternary chlorides

Literature survey on DTA work for elucidating the phase diagrams for Ln=La–Gd

A synopsis of the results of phase diagram investigations up to 1977 is given in the handbook of Gmelin [8] and further in a monograph of Prosypaiko and Allkseeva [9]. However, it must be noted that the literature citation in the Russian monograph is not complete. For example, the publication of Korshunov *et al.* [10], on the systems $KCl/EuCl_3$ and $KCl/TbCl_3$, is missing together with some other important papers. The older investigations were mainly carried out by Russian scientists. All systems with NaCl and KCl, and most with CsCl are described, but only two with RbCl ($RbCl/NdCl_3$ and $RbCl/SmCl_3$). These investigations were performed with the visual-polythermal method, and they contain reliable results for the liquidus curves, namely, for congruently melting compounds. Data about the composition of incongruently melting compounds and about the nature of solid-state reactions, however, are often questionable.

All possible compounds of the type A_3LnCl_6 have been found. However, in no case have formation temperatures for these compounds, which often exist at high temperatures only, been determined. Compounds with the composition A_2LnCl_5 were described only for *A*=Rb and K whereas Cs_2LnCl_5 compounds were not described. The formulation of the Ln richest compounds as ALn_3Cl_{10} is incorrect, it should be ALn_2Cl_7. Exceptions are found in studies of Korshunov on compounds of Sm [11] and Eu [10] and of Frenzel [12] in which the correct composition of KGd_2Cl_7 is not only given but also substantiated. The systems $NaCl/LnCl_3$ (*Ln*=La–Nd) were found as purely eutectical, however, it must be noted that in 1973 Storonkin *et al.* [13] pointed out that $CeCl_3$ seems to dissolve up to 15 mol% NaCl in the solid-state, while Korshunov found incongruently melting compounds in the systems of Sm [10], Eu [14] and Gd [15]. During the last years papers appeared without corrections of older results by Igarashi *et al.* on the systems $NaCl/LaCl_3$ [16], $NaCl/PrCl_3$ [17], $NaCl/NdCl_3$ [18] and $NaCl/GdCl_3$ [19] and by groups in USSR [20, 21] on $NaCl/PrCl_3$. Only Gromov *et al.* [22] for the system $RbCl/CeCl_3$ and Desyatnik *et al.* [23] for the system $KCl/PrCl_3$ got results similar to ours without knowing our investigations.

In the last ten years Chinese papers appeared about the systems $KCl/NdCl_3$ [24] and $NaCl/SmCl_3$ [25], describing one compound in each system, K_3NdCl_6 and Na_2SmCl_5, respectively. An investigation of the system $KCl/CeCl_3$ in 1992 [26] is only partially correct. Wrong findings of Sharma and Rogers on the system $NaCl/NdCl_3$ [27] were corrected in 1998 by Sato and Ogawa [28] who described a compound $Na_3Nd_5Cl_{18}$. A paper about the system $CsCl/PrCl_3$ by Blachnik and Selle [29] will be treated later, in connection with its thermodynamic data.

Results of the phase diagram investigations

Several selected phase diagrams of ternary chlorides are depicted in Figs 1–4. In Table 2 characteristic data for all known ternary chlorides are compiled. They are taken from our own investigations on the phase diagrams of the systems $ACl/LnCl_3$. In column I the highest temperatures of existence of the solid compounds taken from DTA-heating curves are given, melting temperatures (*M*) for congruently melting compounds (like Cs_3LaCl_6 and Rb_3LaCl_6), peritectic temperatures (*P*) for incongruently melting compounds (like ALa_2Cl_7 and Rb_2LaCl_5) and decomposition temperatures (*D*) for compounds which decompose in the solid-state (like Cs_2LaCl_5). In column II temperatures for phase transitions (*T*) between polymorphic modifications (like CsCl, Cs_3LaCl_6, $RbLa_2Cl_7$) or formation temperatures (*F*) for compounds, which are stable only at high temperatures (like Rb_3LaCl_6) are collected. In column III fusion enthalpies are drawn *vp*, finally completed with values measured in 1994 by *Gaune-Escard et al.* [69]. They differ strongly from older values, but are consistent for the whole group. In the last column the names of the principal investigators of the scientific groups who first described the compound are given regardless of correct findings about the existence of solid-state transitions.

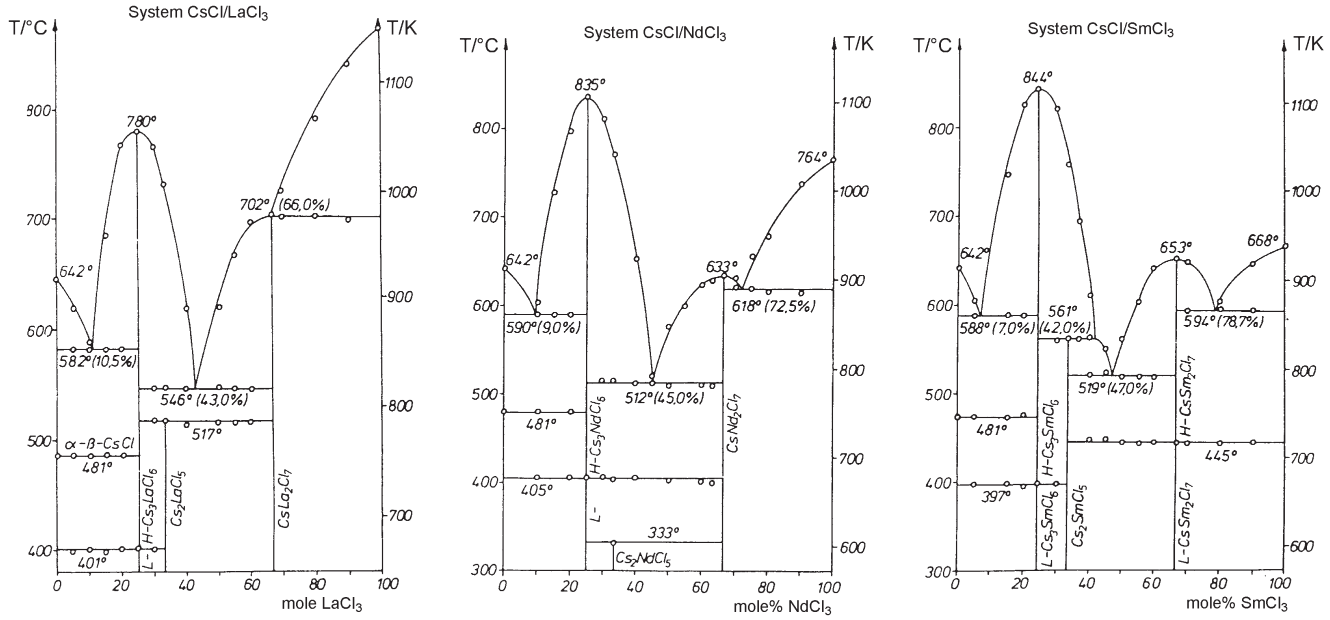


Fig. 1 Phase diagrams CsCl with LaCl$_3$, NdCl$_3$, SmCl$_3$

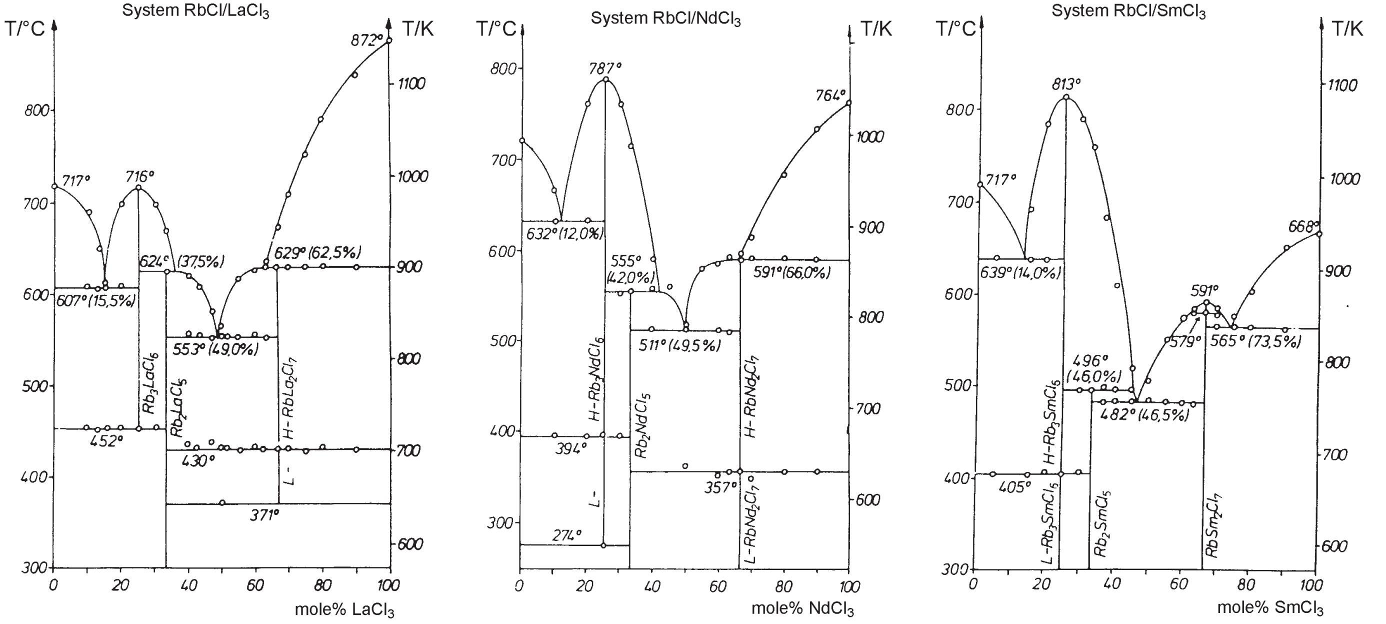


Fig. 2 Phase diagrams, RbCl with LaCl$_3$, NdCl$_3$, SmCl$_3$

Table 2 Characteristic data for ternary chlorides in systems ACl/$LnCl_3$

Compound	I. Highest temperature of existence/K	II. Solid-state transitions/K	III. Fusion enthalpies/ kJ mol^{-1}	IV. Literature
Cs_3LaCl_6	1053 *M*	674 *T*	60.7 [31]; 58.7 [69]	Morozov, 1958 [32]
Cs_2LaCl_5	790 *D*			Seifert, 1985 [1]
$CsLa_2Cl_7$	975 *P*			Seifert, 1985 [1]
Rb_3LaCl_6	989 *M*	717 *F*	50.2 [69]	Seifert, 1985 [1]
Rb_2LaCl_5	897 *P*			Seifert, 1985 [1]
$RbLa_2Cl_7$	902 *P*	703 *T*, 626 *F*		Seifert, 1985 [1]
K_2LaCl_5	913 *M*		104.6 [33]; 78.1 [69]	Novikov, 1961 [34]
$K_3La_5Cl_{18}$	885 *P*	290 *F*		Seifert, 1985 [1]
Mixed cryst. $Na_3La_5Cl_{18}$–$LaCl_3$	~983 *P*			Seifert, 1985 [1]
Cs_3CeCl_6	1077 *M*	674 *T*	67.4 [69]	Morozov, 1958 [32]
Cs_2CeCl_5	716 *D*			Seifert, 1986 [2]
$CsCe_2Cl_7$	952 *M*			Seifert, 1986 [2]
Rb_3CeCl_6	1012 *M*	636 *F*	52.4 [69]	Seifert, 1986 [2] Gromov, 1987 [22]
Rb_2CeCl_5	873 *P*			Seifert, 1986 [2]
$RbCe_2Cl_7$	889 *P*	669 *T* 561 *F*		Seifert, 1986 [2]
K_3CeCl_6	905 *M*	794 *F*	39.1 [69]	Morozov, 1958 [32]
K_2CeCl_5	897 *M*			Morozov, 1958 [32]
$K_3Ce_5Cl_{18}$	807 P	691 *F*		Seifert, 1986 [2]
Mixed cryst. $Na_3Ce_5Cl_{18}$–$CeCl_3$	~913 *P*			Vasilkova, 1973 [13]
Cs_3PrCl_6	1093 *M*	677 *T*	61.1 [69]	Blachnik, 1979 [29]
Cs_2PrCl_5	664 *D*			Seifert, 1987 [3]
$CsPr_2Cl_7$	917 *M*			Blachnik, 1979 [29]
Rb_3PrCl_6	1040 *M*	659 *T* 598 *F*	54.0 [69]	Desyatnik, 1987 [23] Seifert, 1987 [3]
Rb_2PrCl_5	850 *P*			Seifert, 1987 [3]
$RbPr_2Cl_7$	873 *P*	653 *T* 469 *F*		Seifert, 1987 [3]
K_3PrCl_6	945 *M*	754 *F*	84.1 [31]; 48.9 [69]	Morozov, 1960 [35]
K_2PrCl_5	890 *P*			Morozov, 1960 [35]

Table 2 Continued

Compound	I. Highest temperature of existence/K	II. Solid-state transitions/K	III. Fusion enthalpies/ kJ mol^{-1}	IV. Literature
$Na_3Pr_5Cl_{18}$	~873 *P*			Seifert, 1987 [3]
Cs_3NdCl_6	1108 *M*	678 *T*	50.6 [31]; 66.4 [69]	Morozov, 1958 [32]
Cs_2NdCl_5	606 *D*			Seifert, 1988 [4]
$CsNd_2Cl_7$	906 *M*			Seifert, 1988 [4]
Rb_3NdCl_6	1060 *M*	664 *T* 490 *F*	58.8 [69]	Morozov, 1969 [36]
Rb_2NdCl_5	828 *P*			Morozov, 1969 [36]
$RbNd_2Cl_7$	864 *P*	630 *T* 415 *T*		Morozov, 1969 [36]
K_3NdCl_6	972 *M*	714 *F*	94.6 [33] 48.0 [69]	Morozov, 1958 [32, 37]
K_2NdCl_5	883 *P*			Morozov, 1958 [32]
KNd_2Cl_7	783 *P*	731 *F*		Seifert, 1988 [4]
$Na_3Nd_5Cl_{18}$	~813 *P*	~403 *F*		Seifert, 1988 [4]
Cs_3SmCl_6	1117 *M*	670 *T*		Korshunov, 1964 [11]
Cs_2SmCl_5	834 *P*			Seifert, 1988 [5]
$CsSm_2Cl_7$	926 *M*	718 *T*	68.2 [31]	Korshunov, 1964 [11]
Rb_3SmCl_6	1086 *M*	673 *T* 317 *F*		Korshunov, 1964 [11]
Rb_2SmCl_5	769 *P*			Korshunov, 1964 [11]
$RbSm_2Cl_7$	864 *M*	852 *T* 527 *F*		Korshunov, 1964 [11]
K_3SmCl_6	1008 *M*	615 *T* 605 *F*	82.8 [31]	Korshunov, Novikov, 1964 [11, 38]
K_2SmCl_5	839 *P*			Korshunov, Novikov, 1964 [11, 38]
KSm_2Cl_7	818 *M*	553 *F*		Korshunov, Novikov, 1964 [11, 38]
Na_2SmCl_5	704 *P*	423 *F*		Korshunov, 1964 [11]
$Na_3Sm_3Cl_{18}$	692 *P*	354 *F*		Seifert, 1988 [5]
Cs_3EuCl_6	1136 *M*	677 *T*		Seifert, 1989 [6]
Cs_2EuCl_5	859 *P*			Seifert, 1989 [6]
$CsEu_2Cl_7$	932 *M*	708 *T*		Seifert, 1989 [6]
Rb_3EuCl_6	1097 *M*	677 *T*		Seifert, 1989 [6]
Rb_2EuCl_5	723 *D*			Seifert, 1989 [6]
$RbEu_2Cl_7$	871 *M*	848 *T*		Seifert, 1989 [6]

Table 2 Continued

Compound	I. Highest temperature of existence/K	II. Solid-state transitions/K	III. Fusion enthalpies/ kJ mol^{-1}	IV. Literature
K_3EuCl_6	1026 *M*	$\underline{634}$ *T* $\underline{545}$ *F*		Korshunov, 1966 [10]
K_2EuCl_5	818 *P*			Korshunov, 1966 [10]
KEu_2Cl_7	820 *M*	$\underline{432}$ *F*	74.1 [31]	Korshunov, 1966 [10]
Na_3EuCl_6	737 *P*	$\underline{644}$ *F*		Korshunov, 1965 [14]
Na_2EuCl_5	703 *P*	$\underline{342}$ *F*		Korshunov, 1965 [14]
$NaEuCl_4$	679 *P*	$\underline{609}$ *T* $\underline{285}$ *F*		Seifert, 1989 [6]
Cs_3GdCl_6	1146 *M*	673 *T*		Seifert, 1990 [7]
Cs_2GdCl_5	875 *P*			Seifert, 1990 [7]
$CsGd_2Cl_7$	953 *M*	704 *T*		Seifert, 1990 [7]
Rb_3GdCl_6	1113 *M*	683 *T*		Seifert, 1990 [7]
Rb_2GdCl_5	$\underline{667}$ *D*			Seifert, 1990 [7]
$RbGd_2Cl_7$	898 *M*	851 *T*		Seifert, 1990 [7]
K_3GdCl_6	1043 *M*	$\underline{634}$ *T* $\underline{492}$ *F*	97.1 [31]	Korshunov, 1965 [15]
K_2GdCl_5	806 *P*			Korshunov, 1965 [15]
KGd_2Cl_7	846 *M*	825 *T*		Seifert, 1990 [7]
H–Na_3GdCl_6	770 *P*	$\underline{538}$ *F*		Korshunov, 1965 [15]
L–Na_3GdCl_6	*X*	(482 *T*)		Seifert, 1990 [7]
Na_2GdCl_5	703 *P*			Seifert, 1990 [7]
$NaGdCl_4$	703 *M*	556 *T*		Mochinaga, 1988 [19]
$NaGd_xCl_{3x+1}$	695 *P*	$\underline{669}$ *F*		Seifert, 1990 [7]

X=metastable at all temperatures

In DTA curves of phase transitions there are often great differences between reaction temperatures, measured in heating- and cooling-experiments (thermal hysteresis). These are either transitions between modifications, like K_2SO_4-type and K_2NiF_4-type for compounds with the composition A_2MX_4, where the topology of the ions is drastically changed or all formation- and decomposition-reactions. Ions have to move from one site to another through strong potential walls of other ions. This ‘kinetic hindrance’ can be so strong that the reaction fails to occur. While it cannot be detected any longer by DTA measurements, it can be identified by ΔG *vs.* temperature measurements using galvanic cells. (This issue was recently discussed in detail elsewhere [30].)

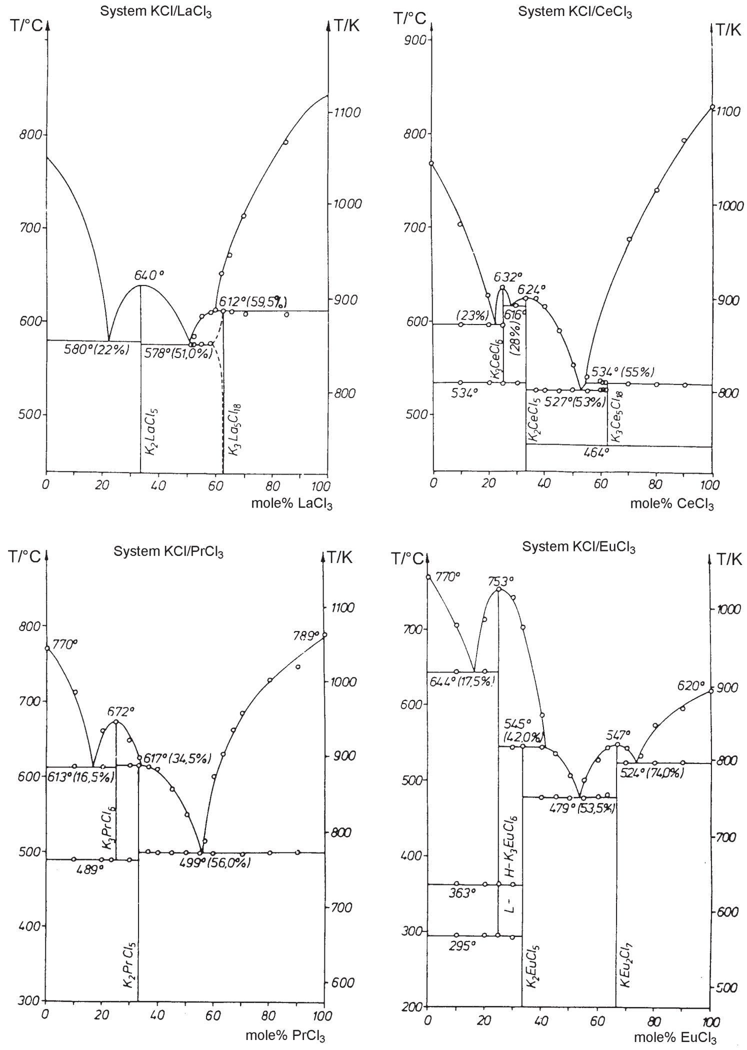


Fig. 3 Phase diagrams KCl with LaCl$_3$, CeCl$_3$, PrCl$_3$, EuCl$_3$

In the second part of this paper the results of these measurements are given. In column II of Table 2 such 'thermodynamic temperatures', measured in galvanic cells, are underlined. They are in general lower than the temperatures from DTA heating-curves and higher than those from cooling-curves.

A peculiar behaviour was found in the system NaCl/GdCl$_3$ [7] (Fig. 4). According to the e.m.f. measurements the compound Na$_3$GdCl$_6$ is stable at temperatures higher than 265°C. Heating a sample, annealed at temperatures between 170 and 250°C, yielded an effect, due to the formation of a compound from NaCl and Na$_2$GdCl$_3$ at ~280–320°C. In cooling experiments a strong undercooling occurred

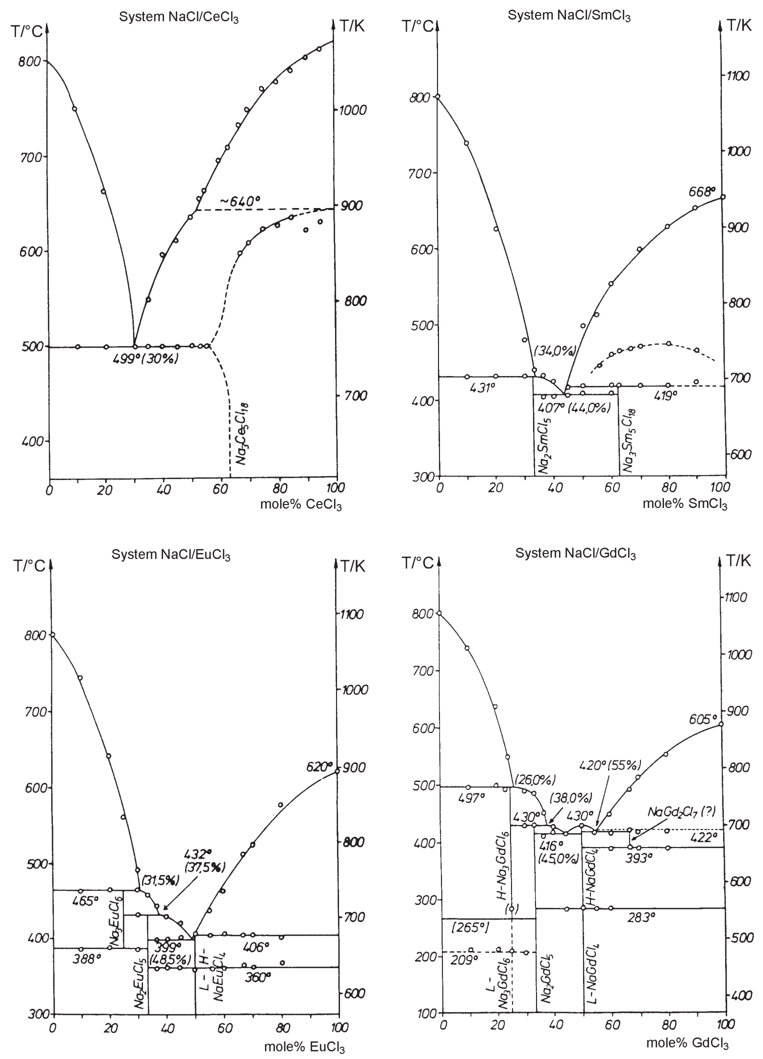


Fig. 4 Phase diagrams NaCl with $CeCl_3$, $SmCl_3$, $EuCl_3$ and $GdCl_3$

and at ~130°C a metastable L–Na_3GdCl_6 was formed. This compound was transformed, when heated to 209°C, to a metastable H–Na_3GdCl_6. That is, the decomposition to NaCl+Na_2GdCl_5 is kinetically hindered and occurs only after annealing. Furthermore, at compositions near 66 mol% $GdCl_3$, from annealed samples containing $NaGdCl_4$ and $GdCl_3$ a high-temperature compound was formed at 393°C, the correct composition of which could not be determined. In Figs 1–4 temperatures are given in °C (left side of the diagram) and in K (right side). The phase transition of CsCl was found between 476 and 486°C. In Fig. 1 a mean value of 481°C is given.

The crystal structures

A synopsis of all the known crystal structures of complex rare-earth halides was given in 1982 by Meyer, based mainly on his own single crystal investigations. More recent information can be found in review articles on phase transitions of lanthanide compounds [39]. In Table 3 unit cell parameters and mole volumes of all actually known structures are compiled. In older literature only tables with peak positions of debyeograms for some ternary chlorides were given [40].

Table 3 Unit cell parameters of ternary lanthanide chlorides

a) High-temperature modification of compounds A_3LnCl_6 (Fm3m, Z=4)

Composition	a/Å	Temp./K	V_M(exp.)	ΣV_M	ΔV_M
Cs_3LaCl_6	11.794	720	247.0	220.8	+26.2
Cs_3CeCl_6	11.834	870	249.5	219.8	+29.7
Cs_3PrCl_6	11.705	770	241.5	218.8	+23.7
Cs_3NdCl_6	11.728	770	242.8	217.7	+25.1
Cs_3SmCl_6	11.620	730	236.2	216.4	+19.8
Cs_3EuCl_6	11.655	770	238.3	215.8	+22.5
Cs_3GdCl_6	11.635	770	237.0	215.3	+21.7
Rb_3LaCl_6	11.532	820	230.9	190.5	+40.4
Rb_3CeCl_6	11.448	770	225.8	189.5	+36.3
Rb_3PrCl_6	11.487	870	228.2	188.5	+39.7
Rb_3NdCl_6	11.343	720	219.7	187.4	+32.3
Rb_3SmCl_6	11.278	720	215.9	186.1	+29.8
Rb_3EuCl_6	11.312	770	218.0	185.5	+32.5
Rb_3GdCl_6	11.289	770	216.5	185.0	+31.5
K_3CeCl_6	11.241	830	213.8	174.5	+39.3
K_3PrCl_6	11.179	870	210.3	173.5	+36.8
K_3NdCl_6	11.143	800	208.3	172.4	+35.9
K_3SmCl_6	11.078	770	204.7	171.1	+33.6
K_3EuCl_6	11.051	770	203.2	170.5	+32.7
K_3GdCl_6	11.025	770	201.7	170.0	+31.7

b) Low-temperature modification of compounds A_3LnCl_6 (A=Cs, Rb; Cs_3BiCl_6-type; C2/c, Z=8)

Composition	a/Å	b/Å	c/Å	β/grad	V_M(exp.)	ΣV_M	ΔV_M
Cs_3LaCl_6	27.286	8.2906	13.3046	99.64	223.4	220.8	+2.6
Cs_3CeCl_6	27.346	8.227	13.329	99.71	223.9	219.8	+4.1
Cs_3PrCl_6	27.209	8.240	13.316	99.87	221.4	218.8	+2.6
Cs_3NdCl_6	27.193	8.248	13.279	99.96	220.8	217.7	+3.1
Cs_3SmCl_6	27.084	8.195	13.202	99.94	217.3	216.4	+0.9

Table 3 Continued

b) Low-temperature modification of compounds A_3LnCl_6 (A=Cs, Rb; Cs_3BiCl_6-type; C2/c, Z=8)

Composition	a/Å	b/Å	c/Å	β/grad	V_M(exp.)	ΣV_M	ΔV_M
Cs_3EuCl_6	27.065	8.192	13.203	99.93	217.1	215.8	+1.3
Cs_3GdCl_6	27.020	8.189	13.181	100.01	216.2	215.3	+0.9
Rb_3LaCl_6	26.171	8.219	12.832	96.49	206.5	190.5	+16.0
Rb_3CeCl_6	26.324	8.073	12.869	98.62	203.6	189.5	+14.1
Rb_3PrCl_6	26.227	8.011	12.885	98.76	201.4	188.5	+12.9
Rb_3NdCl_6	26.139	7.743	13.402	100.65	200.7	187.4	+13.3
Rb_3SmCl_6	26.076	7.703	13.339	100.54	198.3	186.1	+12.2
Rb_3EuCl_6	25.983	7.920	12.928	99.50	197.5	185.5	+12.0
Rb_3GdCl_6	25.917	7.900	12.938	99.52	196.4	185.0	+11.4

c) Low-temperature modification of compounds K_3LnCl_6 (K_3MoCl_6-type; $P2_1/c$, Z=4)

Composition	a/Å	b/Å	c/Å	β/grad.	V_M(exp.)	ΣV_M	ΔV_M
K_3PrCl_6	13.30	7.94	13.01	110.6	193.7	173.5	+20.2
K_3NdCl_6	13.25	7.94	12.98	110.5	192.6	172.4	+20.2
K_3SmCl_6	13.10	7.63	13.07	110.6	184.2	171.1	+13.1
K_3EuCl_6	13.13	7.77	12.69	110.3	182.9	170.5	+12.4
K_3GdCl_6	13.173	7.789	12.688	110.4	183.6	170.0	+13.6

d) Stuffed $LiSbF_6$-structure for Na_3LnCl_6 ($R\bar{3}$; Z=3) [44]

Composition	a/Å	c/Å	V_M(exp.)	ΣV_M	ΔV_M
Na_3EuCl_6	7.018	18.825	161.2	139.6	+21.6
L–Na_3GdCl_6	7.007	18.791	160.4	139.1	+21.3

e) High-temperature modification for Na_3GdCl_6 (cryolithe-structure; $P2_1/n$; Z=2) [43]

Na_3GdCl_6 (275°C)	7.005	7.359	10.356	90.81	160.7	139.1	+21.6

f) Compounds A_2LnCl_5 with the K_2PrCl_5-structure (Pnma-Z=4)

Composition	a/Å	b/Å	c/Å	V_M(exp.)	ΣV_M	ΔV_M
Cs_2LaCl_5 [46]	13.749	9.237	8.531	163.1	168.4	–5.3
Cs_2CeCl_5	13.762	9.208	8.548	163.0	167.4	–4.4
Cs_2PrCl_5	13.729	9.125	8.526	160.8	166.4	–5.6
Cs_2NdCl_5	13.679	9.094	8.502	159.0	165.3	–6.3
Rb_2LaCl_5 [46]	13.146	9.037	8.209	146.8	148.2	–1.4
Rb_2CeCl_5 [46]	13.122	8.985	8.195	145.5	147.2	–1.7
Rb_2PrCl_5 [46]	13.110	8.943	8.181	144.4	146.2	–1.8
Rb_2NdCl_5 [46]	13.111	8.912	8.175	143.8	145.1	–1.3
Rb_2SmCl_5 [46]	13.077	8.844	8.163	142.1	143.8	–1.7

Table 3 Continued

f) Compounds A_2LnCl_5 with the K_2PrCl_5-structure (Pnma-Z=4)

Composition	a/Å	b/Å	c/Å	V_M(exp.)	ΣV_M	ΔV_M
Rb_2EuCl_5 [46]	13.066	8.222	8.158	141.6	143.2	–1.6
Rb_2GdCl_5 [46]	13.066	8.782	8.156	140.9	142.7	–1.8
K_2LaCl_5 [46]	12.742	8.868	8.022	136.5	138.2	–1.7
K_2CeCl_5 [46]	12.717	8.815	7.995	135.0	137.2	–2.2
K_2PrCl_5 [46]	12.710	8.772	7.985	134.0	136.2	–2.2
K_2NdCl_5 [46]	12.707	8.741	7.969	133.3	135.1	–1.8
K_2SmCl_5 [46]	12.676	8.676	7.946	131.6	133.8	–2.2
K_2EuCl_5 [46]	12.664	8.650	7.942	131.0	133.2	–2.2
K_2GdCl_5 [46]	12.651	8.626	7.935	130.4	132.7	–2.3
Na_2SmCl_5	12.040	8.348	7.685	116.2	113.2	+3.0
Na_2EuCl_5	12.044	8.331	7.680	116.0	112.6	+3.4
Na_2GdCl_5	12.031	8.295	7.665	115.1	112.1	+3.0

g) Compounds A_2LnCl_5 with the Cs_2DyCl_5 structure (Pnma-Z=4)

Composition	a/Å	b/Å	c/Å	V_M(exp.)	ΣV_M	ΔV_M
Cs_2SmCl_5	9.618	7.571	15.273	167.4	164.0	+3.4
Cs_2EuCl_5	9.610	7.551	15.232	166.4	163.4	+3.0
Cs_2GdCl_5	9.581	7.514	15.268	165.4	162.9	+2.5

h) Compounds ALn_2Cl_7 with the β-KEr_2F_7-structure (Pna2_1-Z=8)

Composition	a/Å	b/Å	c/Å	V_M(exp.)	ΣV_M	ΔV_M
$CsLa_2Cl_7$	14.964	16.886	9.763	185.6	179.6	+6.2
$CsCe_2Cl_7$	14.883	16.760	9.674	181.6	177.6	+4.0
$CsPr_2Cl_7$	14.83	16.71	9.65	180.0	175.6	+4.4
$CsNd_2Cl_7$	14.808	16.642	9.607	178.2	173.4	+4.8
$RbLa_2Cl_7$	14.825	17.082	9.563	182.3	169.5	+12.8
$RbCe_2Cl_7$	14.683	16.947	9.504	178.0	167.5	+10.5
$RbPr_2Cl_7$	14.61	16.77	9.44	174.1	165.5	+8.6
$RbNd_2Cl_7$	14.631	16.729	9.422	173.6	163.3	+10.3
KNd_2Cl_7	14.458	16.371	9.727	173.3	158.3	+15.0

i) Compounds ALn_2Cl_7 with the $RbDy_2Cl_7$-structure [49] (Pnma-Z=4)

Composition	a/Å	b/Å	c/Å	V_M(exp.)	ΣV_M	ΔV_M
$CsSm_2Cl_7$	13.205	7.099	12.952	182.8	170.8	+12.0
$CsEu_2Cl_7$	13.238	7.073	12.903	181.9	169.6	+12.3
$CsGd_2Cl_7$	13.273	7.047	12.854	181.0	162.9	+12.4
$RbSm_2Cl_7$	12.932	7.024	12.787	174.9	160.7	+14.2

Table 3 Continued

i) Compounds ALn_2Cl_7 with the $RbDy_2Cl_7$-structure [49] (Pnma-Z=4)

Composition	a/Å	b/Å	c/Å	V_M(exp.)	ΣV_M	ΔV_M
$RbEu_2Cl_7$	12.915	7.009	12.772	174.1	159.5	+14.6
$RbGd_2Cl_7$	12.907	6.989	12.735	174.0	158.5	+11.5

j) Compounds KLn_2Cl_7 with the KDy_2Cl_7-structure [49] ($P2_1/a$-Z=4)

Comp.	a/Å	b/Å	c/Å	γ/grad	V_M(exp.)	ΣV_M	ΔV_M
KSm_2Cl_7	12.831	6.947	12.774	89.90	171.4	155.7	+15.7
KEu_2Cl_7	12.804	6.924	12.731	89.77	170.0	154.5	+15.5
KGd_2Cl_7	12.804	6.911	12.703	89.66	169.3	153.5	+15.8

k) Compounds $NaLnCl_4$ in S.G. P $\bar{1}$

Comp.	a/Å	b/Å	c/Å	α/grad	β/grad	γ/grad	V_M(exp.)	ΣV_M	ΔV_M
$NaEuCl_4$ [6]	6.92	6.76	6.53	100.9	91.9	89.8	90.3	85.6	+4.7
$NaGdCl_4$ [50]	7.028	6.763	6.667	100.9	91.7	89.8	93.7	85.1	+8.6

l) Compounds $A_3Ln_5Cl_{18}$ with the $LnCl_3$-structure ($P6_3/m$-Z=1)

Composition	a/Å	c/Å	V_M(exp.)	ΣV_M	ΔV_M
$KLa_{1.67}Cl_6$	7.857	4.309	69.4	71.7	–2.3
$NaLa_{1.67}Cl_6$	7.587	4.368	64.7	66.5	–1.8
$KCe_{1.67}Cl_6$	7.839	4.256	68.2	70.8	–2.6
$NaCe_{1.67}Cl_6$	7.559	4.319	64.3	65.7	–1.4
$NaPr_{1.67}Cl_6$	7.552	4.275	63.6	64.8	–1.2
$NaNd_{1.67}Cl_6$	7.535	4.237	62.7	63.9	–1.2
$NaSm_{1.67}Cl_6$	7.519	4.161	59.4	63.0	–3.6

According to our own investigations with high-temperature Guinier-patterns of crystal powders, all compounds of the type A_3LnCl_6 with A=K, Rb or Cs, crystallize with a cubic pseudoelpasolite-structure at temperatures higher than ~400°C. The chloride ions together with 2/3 of the alkali metal ions form a cubic-close packed structure in which all octahedral holes, formed by Cl^- ions only, are occupied by 1/3 of the A^+ and the Ln^{3+} ions.

In addition to these high-temperature modifications all hexachloro-compounds with Cs and Rb form low-temperature modifications with the monoclinic Cs_3BiCl_6-structure (S.G. C2/c) [41], while the analogous potassium-compounds with Ln=Pr–Gd have the near related K_3MoCl_6-structure (S.G. $P2_1/c$) [42].

In the K_3MoCl_6-structure close packed double layers with a [K]:[Cl] ratio of 1:3 and with all octahedral interstices occupied by Mo^{3+}, alternate with more ‘loose-packed’ double layers with a [K]:[Cl] ratio of 2:3. By this distortion the third K^+ gets a coordination number (CN) higher than 6. Another description of this family was given by Benachenhou *et al.* [41] in a comprehensive paper describing compounds of the type $Cs_{3-x}K_xBiCl_6$. The elpasolite structure (K_2NaAlF_6-type) is described as compact stacking of 'layers of close packed octahedra (MCl_6)', according to an ABC-sequence in the direction of a body diagonal of the cube in Fm3m. All octahedra have a threefold axis parallel to the stacking direction. A prototype is the compound Cs_2KBiCl_6 where the K^+ occupy octahedral holes of the ($BiCl_6$)-lattice and the two Cs^+ accommodate tetrahedral holes. The monoclinic distortion is affected by a 45° rotation of part of the octahedra, so that layers containing octahedra viewed along a twofold axis are formed. The K_3MoCl_6-type reveals an alternation of these two layers with a six-layer sequence, while in the Cs_3BiCl_6-type a twelve-layer sequence exists. A distorted cryolite-structure with a 3L-sequence (S.G. $P2_1/n$) is formed by H–Na_3GdCl_6 [43], while L–Na_3GdCl_6 and Na_3EuCl_6 do not belong to this perovskite-related structure family. According to Meyer [44] they crystallize with a hexagonal cell, derived from a 'stuffed' $LiSbF_6$-structure.

For the compounds A_3LnCl_6 transitions between a cubic H-type and a monoclinic structure are of the non-reconstructive type and there are no significant hystereses between heating and cooling, and therefore the cubic high-temperature phase and cannot be obtained as metastable phase by quenching. As a consequence no single crystals can be obtained. We could determine the site positions for Cs_3LnCl_6 by the Rietveld technique [45]. (In the original papers 1–6 we incorrectly assumed the K_3MoCl_6-structure). It must be pointed out that both structures are formed with an expansion of the mole volume compared with that of the mixture $3ACl+LnCl_3$ and also compared with the total volume of the two compounds ACl and A_2LnCl_5, adjacent in the phase diagrams (defined as neighbour compounds).

For the compounds A_2LnCl_5 Meyer showed that there are two structure families, the K_2PrCl_5-type [46] which contains monocapped trigonal prisms (CN=7) linked to chains via common edges ($[PrCl_3Cl_{4/2}]^{2-}$), and the Cs_2DyCl_5-type [47] in which the coordination of the Ln^{3+} ions is octahedral (*cis*-corner-associated octahedra $[DyCl_4Cl_{2/2}]^{2-}$). The K_2PrCl_5-type is formed from the binary parent compounds accompanied by a loss in mole volume; the compounds are denser packed than all other double chlorides. For the three compounds crystallizing with the Cs_2DyCl_5- structure (Cs_2SmCl_5, Cs_2EuCl_5, Cs_2GdCl_5) the volume is slightly enlarged.

The powder patterns of the double chlorides ALn_2Cl_7 with *Ln*=La, Ce, Pr or Nd, could be indexed analogously to the KEr_2F_7-structure [48], in which the lanthanide ion has the CN 8 (connected antiprism). The compounds with *Ln*=Sm or Eu [49] crystallize either with the orthorhombic $RbDy_2Cl_7$- or with the somewhat disturbed monoclinic KDy_2Cl_7-structure. Both structures are built up of monocapped trigonal prisms [$LnCl_7$], connected via common faces to [Ln_2Cl_{11}] and then via common edges to layers. The mole volumes are increased compared with mixtures of $ACl+2LnCl_3$ and of $1/2A_2LnCl_5+3/2LnCl_3$.

In 1990 Schleid and Meyer determined the structure of $NaGdCl_4$ [50]. The triclinic unit cell (S.G.$P\bar{1}$) may be derived from the fluorite type although both cations, Na^+ and Gd^{3+}, have the CN 7 (monocapped trigonal prisms). (The structure of $LiGdCl_4$ is an inverse chloroscheelite [51].)

A hitherto unknown structure family has the composition $A_3Ln_5Cl_{18}$. It contains two potassium compounds $K_3Ln_5Cl_{18}$ with *Ln*=La or Ce and phases $Na_3Ln_5Cl_{18}$ which are the NaCl-richest points of mixed crystal regions $LnCl_3$/NaCl. In the case of La and Ce a complete range of solid solutions from ~60 mol% $LnCl_3$ to pure $LnCl_3$ exists. For the elements Pr–Sm a miscibility gap is emerging and the phase range is decreasing. Recently Krämer and Meyer [52] has confirmed these findings for the phase $Na_{0.38}(Na_{0.19}Ce_{0.81})Cl_3$. In these compounds the structural motif of the binary compounds $LnCl_3$ (*Ln*=La–Gd; UCl_3-type [53]) is modified by the substitution $[1Ln^{3+}+2\ \text{voids}] \sim 3A^+$. In $LaCl_3$, e.g. each La^{3+} ion is surrounded by a set of six Cl^- ions, defining a trigonal prism, and a set of three Cl^- ions in the equatorial mirror plane of the prism. These 'threefold capped prisms' are connected to $[LaCl_{9/3}]$. For $K_3La_5Cl_{18}$ the structure was determined by single-crystal investigations [1]. The hexagonal unit cell (S.G. $P6_3/m$) contains two units $KLa_{1.67}Cl_6$. In the $LaCl_3$ lattice 1/6 of the La^{3+} sites are statistically occupied by 1/3 of the K^+ and the remaining 2/3 of the K^+ occupy the sites 0,0,0 and 0,0,1/2.

The relations between composition and structure

In all systems with Cs and Rb the same kind of compounds exist (A_3LnCl_6, A_2LnCl_5 and ALn_2Cl_7). The systems with Na are predominated by mixed crystals of NaCl and $LaCl_3$ in the composition range $Na_3Ln_5Cl_{18}$ to $LnCl_3$. The potassium compounds form a transition between both families. At T=0 K the entropy term in the Gibbs–Helmholtz equation becomes zero and stability is controlled by the enthalpies. The lattice enthalpies depend on the fitting of the cations in the voids of the Cl^- packing. Thus, with decreasing the size of the Ln^{3+} ion first the lattice enthalpy increases because the Ln^{3+}–Cl^- distance becomes smaller until a 'critical radii relation' is reached, then a transition to a structure type with a smaller CN occurs. The radii of the Ln^{3+} ions [54] decrease from La^{3+} (100.1 pm) to Gd^{3+} (95.0 pm). This leads to decreasing tendency of occupying interstices of the CN 7 in the Cl^- packing in favour of an octahedral coordination.

With decreasing distance the complete $LnCl_x$ polyhedra get smaller and thus also the voids in the Cl^- packing are shrinking, so that at last the A^+ ions become too big for the given structure type. From Cs^+ to Na^+ the tendency for formation of the CN 6 of the alkali ions increases. The CN in the main structure types are:

	Cs_3LnCl_6	K_2PrCl_5	Cs_2DyCl_5	KEr_2F_7	$RbDy_2Cl_7$
CN for Ln^{3+}	6	7	6	8	7
CN for A^+	2×2+1×6	8	10/11	9/11	(10+2)

At elevated temperatures a higher symmetry exists caused by the higher temperature motion of the ions. For all groups of compounds the volumes of the unit cells diminish from La to Gd due to the diminishing ionic radii. For the same reason Rb-compounds form smaller unit cells compared with Cs-compounds of the same composition.

The compounds A_3LnCl_6

Cubic elpasolites A_3LnCl_6 exist at high temperatures with all lanthanides. Among the low-temperature modifications with the monoclinic Cs_3BiCl_6-structure (S.G. C2/c), or the near related K_3MoCl_6-structures, (S.G. $P2_1/c$) only Cs- and Rb-compounds of Sm, Eu and Gd are stable at ambient temperature. The stability range of the compounds Rb_3PrCl_6, Rb_3NdCl_6 and K_3GdCl_6 lies between ~280 and ~380°C, while L–K_3SmCl_6 exists only between 338 and 354°C. By quenching from these temperatures these compounds can be maintained at room temperature but they are metastable. L–Rb_3LnCl_6 with *Ln*=La or Ce and L–K_3LnCl_6 with *Ln*=Pr or Nd are metastable at all temperatures. They are formed when quenching the cubic high-temperature modifications.

An explanation for these relations is based on the following rules. Lanthanide ions, the smaller they are, the better they fit into octahedral interstices of closed packed Cl^- ions. Thus, the temperature ranges of stability increase from La^{3+} to Eu^{3+}. The alkali ions have CN $\{2\times12+1\times6\}$ in the elpasolite type and only 8 in the Cs_3BiCl_6-type, which therefore is the low-temperature modification. Since CN is >6 the desired CN for Rb^+ and K^+ in both modifications of A_3LnCl_6 compounds have decreasing regions of existence when going from Cs- to Rb-compounds. The situation is still worse for K-compounds. They crystallize with the K_3MoCl_6-structure, which is very similar to the Cs_3BiCl_6-type. K^+ ions can become six coordinated only if Cl^- packing shrinks, and this can happen to small Ln^{3+} ions. Thus, the first compound K_3LnCl_6 with elpasolite structure exists (above 543°C) with *Ln*=Ce. The first stable example with K_3MoCl_6-structure is K_3SmCl_6 (338 to 354°C).

Finally, europium and gadolinium form compounds Na_3EuCl_6 and L–Na_3GdCl_6 with a ‘stuffed $LiSbCl_6$‘-structure. Na^+ and Eu^{3+} occupy slightly distorted octahedral holes in a hexagonal close-packed chloride framework. H–Na_3GdCl_6 has the cryolite structure, a monoclinic, pseudo-cubic face-centered lattice, where Gd has a somewhat distorted octahedral surrounding of Cl^- ions. Thus, in all these sodium compounds CN of Ln^{3+} and A^+ is 6.

The compounds A_2LnCl_5

All K- and Rb-compounds crystallize with K_2PrCl_5-structure, CNs of Ln^{3+} and A^+ ions are 7 and 8+1, respectively. With decreasing lanthanide radius, $r(Ln^{3+})$, the unit cells as well as Cl–Cl-distances become smaller. Consequently, beginning with samarium, also the sodium ions fit into the bis- to tri-capped (CN 8+1) trigonal prisms of K_2PrCl_5-type and the compounds Na_2LnCl_5 (*Ln*=Sm, Eu or Gd) are formed.

On the other hand, the interstices in the chloride prism become too small for the bigger A^+ ions. That occurs to Rb^+ with elements behind gadolinium and the 2:1-compounds with Tb^{3+} [55] and Dy^{3+} [56] no longer exist. For Cs-compounds the situation is different. Here Cl^- packing of K_2PrCl_5-type becomes too small for Cs^+ in the samarium-compound. Cs_2SmCl_5 and the following compounds crystallize with Cs_2DyCl_5-structure, where the CN of Cs^+ in connected octahedra of $[LnCl_4Cl_{2/2}]^{2+}$ becomes 10+1.

Table 4 Solution enthalpies (kJ mol^{-1}) of lanthanide trichlorides with UCl_3-structure in 10^{-3} M HCl and alkalimetal chlorides in $LnCl_3$-solutions (dilution 1:6000)

Compound	$\Delta H^0_{sol\ 298}$	Literature	Compound	$\Delta H^0_{sol\ 298}$	Literature
$LaCl_3$	–134.6(6)	–131.0 to –137.8	$SmCl_3$	–164.7(2)	–163.2 to –167.1
$CeCl_3$	–138.9(8)	–136.8 to –144.0	$EuCl_3$	–171.5(3)	–170.3 to –174.9
$PrCl_3$	–145.8(5)	–141.5 to –149.2	$GdCl_3$	–180.3(5)	–177.4 to –181.8
$NdCl_3$	–149.5(4)	–147.7 to –153.3	$TbCl_3$	–188.8(4)	–186.9 to –191.8
			$DyCl_3$	–197.1(3)	~ –198
CsCl: 18:1(2)		RbCl: 17.6(2)	KCl: 17.9(1)	NaCl: 4.5(1)	

The compounds ALn_2Cl_7

The structural relations among the compounds ALn_2Cl_7 are simpler than those of the 2:1-compounds. The lanthanides from La^{3+} to Nd^{3+} form with Cs^+- and Rb^+-compounds of the KEr_2F_7-type, where CN for Ln^{3+} ions is 8 and that of the alkali metal ions 9 and 11. With the smaller potassium ion only one compound, KNd_2Cl_7, exists which is stable in the small temperature range 493 to 510°C. From Sm to Gd the three bigger alkali metal ions (Cs, Rb, K) form 1:2-compounds with the $RbDy_2Cl_7$- or KDy_2Cl_7-structure. CN of Ln^{3+} is now 7 and those of A^+ ions are (10+2). For Na^+ this CN is very high, thus only one compound, $NaGd_2Cl_7$, exists in a small temperature range from 399 to 423°C. It must be pointed out, that, in several systems, high-temperature modifications of ALn_2Cl_7 exist, but their structure is not known.

The mixed-crystal phases $LnCl_3$–$Na_3Ln_5Cl_{18}$

Ternary chlorides with the composition $A_3Ln_5Cl_{18}$ were found with *A*=Na in systems of *Ln*=La–Sm and with *A*=K in systems of *Ln*=La or Ce. As already explained, they can be derived from the binary compounds $LnCl_3$ (*Ln*=La–Gd), which have the hexagonal UCl_3-structure. The whole arrangement can also be described starting from a strongly distorted hexagonal close packing of Cl^- ions. Part of Ln^{3+} ions, up to a sixth, can be statistically substituted by A^+ ions of comparable size. For electroneutrality two other A^+ occupy part of the quasi-octahedral holes in 0,0,0 and 0,0,1/2. In the optimal case, that is the system $NaCl/CeCl_3$ [2], we found a miscibility area from $CeCl_3$ to ~$Na_3Ce_5Cl_{18}$. Here $r(Ce^{3+})$ is 103 pm and $r(Na^+)$ is 102 pm. The hexagonal unit cell of $CeCl_3$ is widened in the *a*-direction, while the lattice constant *c* is nearly independent of the degree of mixed crystal formation. We have two 'vegard-lines', as shown in

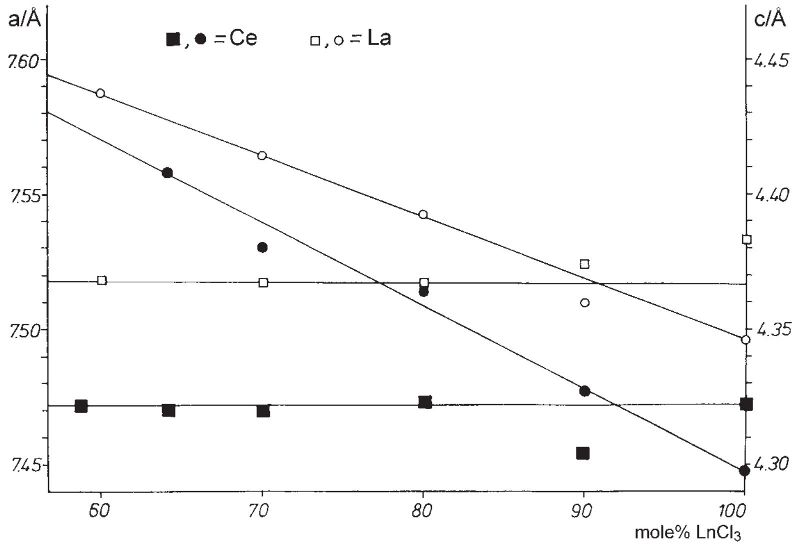


Fig. 5 Vegard's line for $NaLn_{1.67}Cl_6$ (*Ln*=La, Ce [2])

Fig. 5. For the elements Pr–Sm the miscibility gap is emerging while the phase range is decreasing.

Thermodynamic properties

Why do ternary chlorides exist?

This question was recently discussed in detail in this journal [57]. Classical thermodynamics tells us that in a system $ACl/LnCl_3$ in chemical equilibrium, the Gibbs free energy of formation of a ternary chloride from the two adjacent compounds in the phase diagram (neighbour compounds), the free enthalpy of synproportionation, ΔG^0_{syn}, must be negative. For example, the compound Cs_2LaCl_5 in the system $CsCl/LaCl_3$ (Fig. 1) must be formed from Cs_3LaCl_6 and $CsLa_2Cl_7$ according to the equation $0.6\ Cs_3LaCl_6+0.4\ Cs_{0.5}LaCl_{3.5}=Cs_2LaCl_5$ by a gain in ΔG. This free enthalpy is related to the enthalpy ΔH by the Gibbs–Helmholtz relation, $\Delta G=\Delta H-T\Delta S$. At T=0 K a compound can be stable only if ΔH^0 is negative as well. As the thermodynamic cycle in Fig. 6 demonstrates, ΔH^0 is identical with a change in lattice energy compared with the two neighbour compounds. At higher temperatures also the entropy term, $T\Delta S^0$, becomes more and more influential. In solid-state chemistry it is often assumed that the entropy change in solid reactions is negligible, so that the claim of exothermic reactions can also be applied to ambient temperature.

We found in numerous systems of ACl/MCl_2 and ACl/MCl_3 that the enthalpies of synproportionation, ΔH^0_{syn}, are in general small compared with the absolute value of lattice enthalpy, 0.1–30 kJ compared with more than 1000 kJ, respectively. Thus, the $T\Delta S$ term at higher temperatures may become sufficiently high to compensate a loss in lattice enthalpy. We found several groups of compounds, which exist due to entropy only at elevated temperature (e.g. Rb_3LaCl_6 in Fig. 2).

ΔG values can be determined by e.m.f. measurements of the reaction nACl+$A_mLnCl_{m+3}=A_{(m+n)}LnCl_{(m+n+3)}$ in galvanic chlorine cells for solid electrolytes [58], using the relation $\Delta G=-n$FE. For Rb_3LaCl_5, for instance, the electrolytes are RbCl and Rb_2LaCl_5, separated by a Rb^+ conducting diaphragm. First we constructed such cells with diaphragms for A=Na, K or Rb. Later we found a material, based on β-alumina, which allows the measurements for Cs-rich compounds too. In all cases the dependence of the e.m.f. on temperature proved to be linear at ≥250°C, so that a regression line $E=a+bT$ could be transformed directly to $\Delta G=\Delta H-T\Delta S$, indicating that ΔH and ΔS are temperature-independent in the range of measurement.

A direct measurement of ΔH at ambient temperature is possible by solution calorimetry. We made such measurements with a home-built isoperibolic calorimeter [59]. The correlation between both measurements of ΔH is not excellent, but is acceptable (Δ up to maximum 4 kJ mol^{-1}). One has to take into account that linearity, which means that ΔH is independent of T, must not hold down to ambient temperature. Here Δc_p-measurements are necessary to explain the differences in ΔH. Among Cs-compounds only Cs_3LnCl_6 has been studied by e.m.f. measurement until now. The stability of these compounds is therefore discussed in the next section with the results of solution calorimetry. For the other compounds the stability discussion is given together with results of e.m.f. measurements. Here the values from solution calorimetry have a control function only.

Results from solution calorimetry

The first measurements in this field were conducted by Baev and Novikov [34] in 1961. However, they did not know the exact phase diagrams and, therefore, most of their measurements were made with mixtures (e.g. $3KCl\cdot2CeCl_3$, is actually a mixture of K_2CeCl_5 and $CeCl_3$). Only the value for K_2LaCl_5 is useful and is in good agreement with our own findings. Other compounds, K_3LnCl_6 (with *Ln*=Ce, Pr or Nd) are stable only at temperatures higher than at least 450°C and, therefore, decompose to $KCl+K_2LnCl_5$ during cooling. Once again the measured values are not useful and instead of negative ΔH_f^0 the correct formation enthalpies from $3KCl+LnCl_3$ are positive, as we have found by e.m.f. measurements. The same holds for the measurements of these compounds by Blachnik and Selle [60]. Their results with other substances K_2LnCl_6, KLn_2Cl_7 and Cs_3LnCl_6 agree fairly well with ours. Only with some $CsLn_2Cl_7$ compounds the difference in enthalpy between our and their results is greater than 5%.

The binary compounds $LnCl_3$ and ACl

In Table 4 our measurements of solution enthalpies of the trichlorides $LnCl_3$ (*Ln*=La–Tb) [61] are compiled together with data from a review article of Burgess and Kijowski [62]. (In [61] results of our measurements of the solution enthalpies of all existing hydrates $LnCl_3\cdot nH_2O$ are also given.) A recent measured value of $-166.97+1.10$ kJ mol^{-1} for $EuCl_3$ [63] is extremely low. Hennig *et al.* [64] measured a value of -146.9 kJ mol^{-1} in 4 M HCl. Together with the measured value of Eu_2O_3 in HCl and enthalpies from tables the calculated formation enthalpy, ΔH_f^0, of $EuCl_3(s)$ at 298 K is equal to -913.3 ± 3 kJ mol^{-1}. Earlier, Oppermann determined several thermodynamic quantities of La, Nd, Sm and Y trichlorides. Measurements of $LaCl_3$ and $CeCl_3$ by the group of Cordfunke and Boji [65] gave values in rather good agreement. They used the solution enthalpy of the lanthanide metals in hydrochloric acid for the thermodynamic calculation cycles.

There is a distinct kink in the curve of solution-enthalpy *vs.* atomic number between neodymium and samarium. According to Spedding *et al.* [66] this is caused by a change in the coordination number of the hydrated ions. The coordination number is 9 from La^{3+} to Nd^{3+} and changes to 8 from Gd^{3+} to Er^{3+}. Their interpretation is based on partial molar volume that they calculated from specific mass measurements of $LnCl_3$ solutions. Between Nd and Gd a ‘displacement equilibrium’ occurs. Blachnik and Selle [29] came to an analogous result when deriving hydration enthalpies of Ln^{3+} ions from solution calorimetry of the compounds A_3LnCl_6 and ALn_2Cl_7. They found a ‘tetradic effect’, La, Ce, Pr, Nd form a first tetrad and Pm to Tb a second. However, they had no experimental values for Pm, Eu and Tb.

It must be pointed out that this kink originated by the situation in the solution and does not stem from the relations in solid $LnCl_3$ as the lattice enthalpies change monotonously from $LaCl_3$ (–4273 kJ mol^{-1}) to $GdCl_3$ (–4453 kJ mol^{-1}) [67] as expected from the decreasing unit cell volume of the trichlorides.

Cs-compounds

In Table 5 the solution enthalpies of three groups of compounds, Cs_3LnCl_6, Cs_2LnCl_5 and $Cs_{0.5}LnCl_{3.5}$, are compiled in the second column. In the third column the enthalpies for the formation-reactions from the binary parent-compounds are given: nACl+$LnCl_3$=A_nLnCl_{3+n}. They are calculated from the solution enthalpies:

$$\Delta H^0_{\mathrm{f}\,298}=\{\Delta H^0_{\mathrm{sol}\,298}(\mathrm{LnCl_3})+n\Delta H^0_{\mathrm{sol}\,298}(\mathrm{ACl})\}-\Delta H^0_{\mathrm{sol}\,298}(\mathrm{A_nLnCl_{3+n}})$$

Table 5 Solution enthalpies and related enthalpy values (kJ mol^{-1}) of Cs-compounds

Comp.	$\Delta H^0_{\mathrm{sol}\,298}$	$\Delta H^0_{\mathrm{f}\,298}$	$\Delta H^0_{\mathrm{syn}\,298}$	Comp.	$\Delta H^0_{\mathrm{sol}\,298}$	$\Delta H^0_{\mathrm{f}\,298}$	$\Delta H^0_{\mathrm{syn}\,298}$
Cs_3LaCl_6	–65.5(9)	–14.8	+18.5	Cs_2LaCl_5	–65.1(3)	–33.3	–21.7*
Cs_3CeCl_6	–58.4(7)	–26.0	+9.9	Cs_2CeCl_5	–66.8(6)	–35.9	–16.9
Cs_3PrCl_6	–57.1(1)	–34.4	+5.0	Cs_2PrCl_5	–70.2(5)	–39.4	–13.9*
Cs_3NdCl_6	–56.3(6)	–38.9	–1.7*	Cs_2NdCl_5	–76.1(3)*	–37.2*	–9.0*
Cs_3SmCl_6	–54.1(2)	–56.3	–21.5*	Cs_2SmCl_5	–93.7(5)	–34.8	+6.2
Cs_3EuCl_6	–57.3(2)	–59.9	–18.8	Cs_2EuCl_5	–94.2(6)	–41.1	+2.6
Cs_3GdCl_6	–59.3(2)	–66.7	–20.3	Cs_2GdCl_5	–97.7(4)	–46.4	+2.8
$\frac{1}{2}CsLa_2Cl_7$	–118.9(4)*	–6.7*	+1.6*	Terbium and dysprosium compounds			
$\frac{1}{2}CsCe_2Cl_7$	–121.5(8)	–8.4	+0.6	Cs_3TbCl_6	–61.0(3)	–73.5	–16.0
$\frac{1}{2}CsPr_2Cl_7$	–124.6(2)	–12.2	–2.3	Cs_3DyCl_6	–58.2(1)	–86.2	–14.4
$\frac{1}{2}CsNd_2Cl_7$	–128.1(5)	–12.4	–3.1*	Cs_2TbCl_5	–95.1(4)	–57.5	–1.9
$\frac{1}{2}CsSm_2Cl_7$	–137.8(9)	–17.9	–9.2	Cs_2DyCl_5	–90.2(9)	–71.8	–6.9
$\frac{1}{2}CsEu_2Cl_7$	–143.0(3)	–19.5	–9.2	$\frac{1}{2}CsTb_2Cl_7$	–151.4(7)	–28.3	–13.7
$\frac{1}{2}CsGd_2Cl_7$	–148.2(6)	–23.0	–11.4	$\frac{1}{2}CsDy_2Cl_2$	–155.4(2)	–32.9	–14.9

In the last column enthalpies of synproportionation $\Delta H^0_{\mathrm{syn}\,298}$ are shown. They belong to the reactions:

$$CsCl+Cs_2LnCl_5=Cs_3LnCl_6$$

$$0.6Cs_3LnCl_6+0.4Cs_{0.5}LnCl_{3.5}=Cs_2LnCl_5$$

$$0.25Cs_2LnCl_5+0.75LnCl_3=Cs_{0.5}LnCl_{3.5}$$

When working out this compilation in some cases measurements or calculations had to be repeated, and may differ from the original publications. They are marked by an asterisk.

Compounds Cs_3LnCl_6 show a maximum in the curve of the solution enthalpies *vs.* atomic number at Cs_3SmCl_6 attributed to the same effect as the kink shown by the compounds $LnCl_3$. The change in formation enthalpy, ΔH_f^0, from CsCl and $LnCl_3$, is strongly increasing. A more profound discussion is given later, because recently we [68] were able to measure e.m.f. *vs.* temperature curves for the synproportionation $CsCl+Cs_2LnCl_5=Cs_3LnCl_6$.

For the compounds Cs_2LnCl_5 and $CsLn_2Cl_7$ the situation is different. Here a change of crystal structures occurs between the Nd and Sm compounds, from the K_2PrCl_5- to the Cs_2DyCl_5- and from the KEr_2F_7- to the $RbDy_2Cl_7$-type, respectively. This has a pronounced effect on the synproportionation enthalpies.

Solution enthalpies of Rb-, K- and Na-compounds of the type A_3LnCl_6, A_2LnCl_5 and ALn_2Cl_7

For all rubidium and potassium compounds free enthalpies, ΔG^0, could be obtained by e.m.f. measurements. These values are compiled and discussed together with the variations of enthalpies and entropies in the next section. Therefore in Table 6 only solution enthalpies are given. Again, corrected values are noted by asterisk. For high temperature compounds which could not be quenched to ambient temperature without partial decomposition, for example, compounds Rb_3LnCl_6 with *Ln*=La–Pr, no solution enthalpies could be measured.

Table 6 Solution enthalpies (kJ mol^{-1}) of Rb-, K- and Na-compounds

	Compounds A_3LnCl_6		Compounds A_2LnCl_5			Compounds ALn_2Cl_7	
Ln	Rb	K	Rb	K	Na	Rb	K
La	–	–	–66.0(5)	–73.9(5)	–	–124.3(8)*	–
Ce	–	–	–65.1(8)	–75.8(9)	–	–128.2(6)	–
Pr	–	–	–67.9(4)	–76.0(3)	–	–133.8(5)*	–
Nd	–74.8(8)	–	–71.0(3)	–80.7(3)	–	–136.4(4)	–143.7(2)
Sm	–71.6(5)	–96.5(8)	–73.3(1)	–87.7(5)	–170.1(2)	–141.1(4)	–153.7(3)
Eu	–73.2(2)	–97.6(8)	–75.2(2)	–92.3(5)	–173.2(2)	–148.7(1)	–157.3(7)
Gd	–75.5(3)	–97.4(6)	–91.4(6)	–96.7(6)	–180.1(3)	–155.1(4)	–162.1(2)
Dy	–75.9(4)	–103.3(3)	–	–104.8(3)	(–)	–163.6(1)	–167.2(3)

Miscellaneous K- and Na-compounds

For the lanthanides La–Sm sodium compounds Na_5LnCl_{18} and for La and Ce analogous potassium compounds exist as well. They can be derived by substitution of one Ln^{3+} in $(LnCl_6)_6$ by three A^+ ions of a similar radius and are therefore parts of extended mixed crystal areas for the systems $NaCl/LnCl_3$ (*Ln*=La–Pr). For the two K-compounds and for the compounds $Na_3Ln_5Cl_{18}$ (*Ln*=Nd or Sm) the composition range is small or negligible. Therefore, also e.m.f.-measurements could be performed for them (see next section). In

Table 7 solution and formation enthalpies are given. For Na-compounds (except $Na_3Sm_5Cl_{18}$) these ΔH_f values are identical with the 'synproportionation' enthalpies because they are the unit compounds in their systems. All these values are positive, that is, these mixed-crystal phases exist only at elevated temperatures.

Table 7 Solution and formation enthalpies (kJ mol^{-1}) from ACl+$LnCl_3$ for compounds 1/5($A_3Ln_5Cl_{18}$)

Compound	$\Delta H^0_{sol\,298}$	$\Delta H^0_{f\,298}$	Compound	$\Delta H^0_{sol\,298}$	$\Delta H^0_{f\,298}$
$Na_{0.6}LaCl_{3.6}$	–135.5(6)	+5.4	$K_{0.6}LaCl_{3.6}$	–113.6(4)	–6.8
$Na_{0.6}CeCl_{3.6}$	–	–	$K_{0.6}CeCl_{3.6}$	–123.2(8)	–5.0
$Na_{0.6}PrCl_{3.6}$	–149.0(8)*	+6.0*			
$Na_{0.6}NdCl_{3.6}$	–153.3(6)	+6.5			
$Na_{0.6}SmCl_{3.6}$	–166.7(7)	+4.7			

Beginning with Eu compounds of the type $NaLnCl_4$ also exist. Their solution enthalpies are:

$$\Delta H^0_{sol\,298}\ (L\text{–}NaEuCl_4) = -172.0(2)\ \text{kJ mol}^{-1};$$

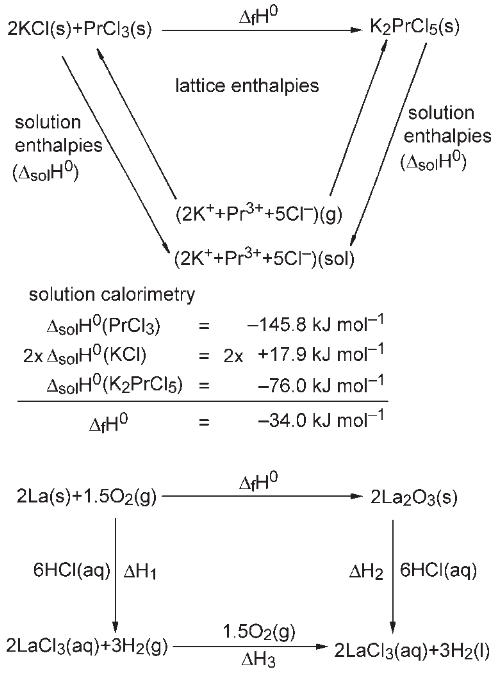
$$\Delta H^0_{sol\,298}\ (NaGdCl_4) = -187.0(4)\ \text{kJ mol}^{-1};$$

$$\Delta H^0_{sol\,298}\ (H\text{–}NaEuCl_4) = -176.0(5)\ \text{kJ mol}^{-1}.$$

E.m.f. measurements

As explained in 'Why do ternary chlorides exist?' one can obtain all thermodynamic functions for the formation of a ternary chloride from the binary parent compounds and also from the adjacent compounds by measuring e.m.f. values with galvanic cells in which these solid-state reactions occur. A detailed description of such cells is given in [58] and the results obtained for lanthanides in [1] to [7]. Measurements were possible at temperatures higher than 250°C. In all cases the dependency of the e.m.f. measurement on temperature was linear, so that the regression lines e.m.f.=$a+bT$ could directly be transformed to the Gibbs–Helmholtz relation with temperature-independent ΔH^0 and ΔS^0. The whole procedure was published in this journal in 1986 [2], describing the system RbCl/$CeCl_3$ as an example.

In this system (Fig. 7) the three compounds $RbCe_2Cl_7$, Rb_2CeCl_5 and Rb_3CeCl_6 exist. The cell for the e.m.f. measurements of the reaction 0.5 RbCl+$CeCl_3$= $Rb_{0.5}CeCl_{3.5}$ was built up from discs of RbCl *vs.* mixtures with 95 mol% $CeCl_3$ and 70 mol% $CeCl_3$, respectively. Approximately 30 pairs of values were measured for each run in the temperature range 630 to 730 K. The mean of both calculated regression lines gave: e.m.f./mV=41.5+0.3213 T/K. Multiplying by 0.5 F (F=Faraday constant) results in the Gibbs–Helmholtz equation, ΔG^0_f/kJ mol^{-1}=–2.0–0.0155 T/K. The accuracy for ΔG^0_f is ±0.4 kJ mol^{-1}. The two constants are: ΔH^0_f=–2.0±0.3 kJ mol^{-1} and ΔS^0_f=15.5±0.5



solution calorimetry

$\Delta_{sol}H^0(PrCl_3)$ = −145.8 kJ mol^{-1}

2x $\Delta_{sol}H^0(KCl)$ = 2x +17.9 kJ mol^{-1}

$\Delta_{sol}H^0(K_2PrCl_5)$ = −76.0 kJ mol^{-1}

Δ_fH^0 = −34.0 kJ mol^{-1}

Fig. 6 Energy values for the formation of K_2PrCl_5 [3]

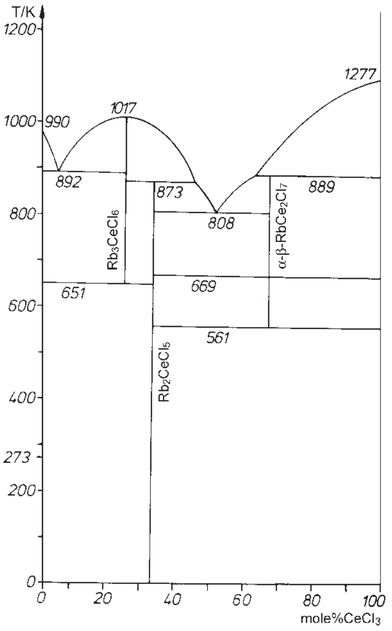


Fig. 7 System RbCl/$CeCl_3$

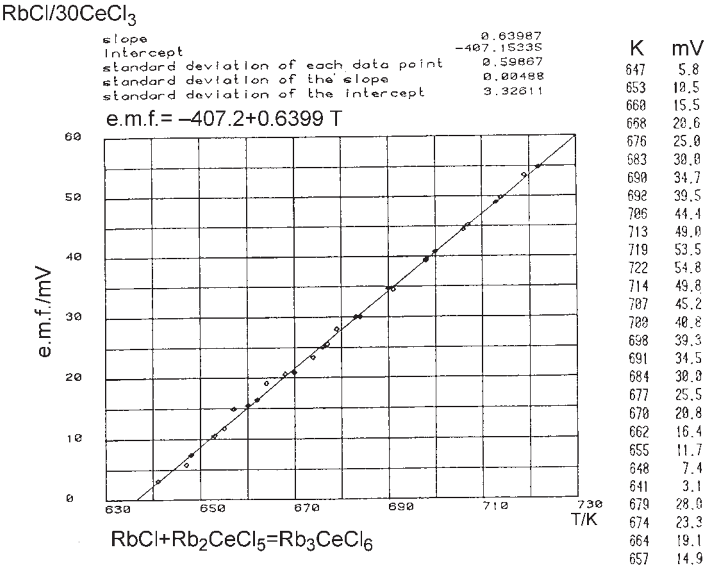
J K^{-1} mol^{-1}. The enthalpy for the phase transition at 669 K (396°C) must be so small, that no kink in the regression line could be detected. Another situation was found for a phase transition of Rb_3SmCl_6, as depicted in [5].

For the reaction $1.5RbCl+Rb_{0.5}CeCl_{3.5}=2Rb_2CeCl_5$ two samples with 60 and 45 mol% $CeCl_3$ were used. The mean regression line is e.m.f./mV=244.7–0.0412 T/K. Multiplying by 1.5 F gives ΔG_r^0/kJ mol^{-1}= –35.4+0.0060 T/K. The slope of the e.m.f. *vs.* temperature-line is now negative giving a negative reaction entropy, ΔS_r^0= –6.0±0.5 J K^{-1} mol^{-1}. To obtain the functions for the reaction $2RbCl+CeCl_3$= $2Rb_2CeCl_5$, the ΔG_r^0 value for the formation of $Rb_{0.5}CsCl_{3.5}$ must be added, so that $\Delta_f G^0$/kJ mol^{-1}= –37.4–0.0095 T/K.

For the reaction $RbCl+Rb_2CeCl_5=Rb_3CeCl_6$ two samples with 30 mol% were used. A computer plot of the measured values of one run is shown in Fig. 8. Multiplication of the mean regression line with 1 F gives: $\Delta_r G$/kJ mol^{-1}=+38.2–0.0601 T/K. It follows, that ΔG^0=0 at 636 K. That is, Rb_3CeCl_6 is stable only at temperatures ≥636 K. This can be seen directly from the computer plot, as well. For the formation of a compound from $3RbCl+CeCl_3$ the Gibbs–Helmholtz relation is ΔG_f^0/kJ mol^{-1}=+0.8–0.0506 T/K. In Table 8 enthalpies and entropies for the formation of all Rb-, K- and Na-compounds from binary compounds are compiled, together with values of ΔG_f^0 for 573 K and ΔH_f^0 values, measured by solution calorimetry.

Free synproportionation enthalpies and stabilities

The stability of a ternary compound in a quasi-binary system is given by the free enthalpy of formation from the two adjacent compounds, which is called 'free



```
slope                                          0.63987
Intercept                                   -407.15335
standard deviation of each data point          0.59867
standard deviation of the slope                0.00488
standard deviation of the intercept            3.32611
```

K	mV
647	5.8
653	10.5
660	15.5
668	20.6
676	25.0
683	30.0
690	34.7
692	39.5
706	44.4
713	49.0
719	53.5
722	54.8
714	49.8
707	45.2
700	40.8
698	39.3
691	34.5
684	30.0
677	25.5
670	20.8
662	16.4
655	11.7
648	7.4
641	3.1
679	28.0
674	23.3
664	19.1
657	14.9

Fig. 8 Computer plot e.m.f. *vs.* T for Rb_3CeCl_6

synproportionation enthalpy' ΔG^0_{syn}. Taking again the system RbCl/CeCl$_3$ as an example, these are ΔG^0_r values for the formation reaction of Rb$_{0.5}$CeCl$_{3.5}$ from Rb$_2$CeCl$_5$ and CeCl$_3$, of Rb$_2$CeCl$_5$ from Rb$_3$CeCl$_6$ and Rb$_{0.5}$CeCl$_{3.5}$ and of Rb$_3$CeCl$_6$ from RbCl and Rb$_2$CeCl$_5$. With ΔG^0_{syn}=0 the temperature of formation (or decomposition) from (or to) the two neighbours is determined. For the system RbCl/CeCl$_3$ the diagram, given in Fig. 8, shows that only the compound Rb$_2$CeCl$_5$ is stable down to 0 K. The two other compounds are 'high temperature phases' relative to zero. Thus, the stability criterion for Rb$_2$CeCl$_5$ is the function ΔG^0_f, given by the reaction 2RbCl+CeCl$_3$=Rb$_2$CeCl$_5$. These values are given in Table 8.

The equations for the synproportionation reactions of the two other compounds are:

1/4Rb$_2$CeCl$_5$+3/4CeCl$_3$=Rb$_{0.5}$CeCl$_{3.5}$ ΔG^0_{syn}/kJ=7.4–0.0131 T/K; ΔG^0=0 at 561 K

RbCl+Rb$_2$CeCl$_5$=Rb$_3$CeCl$_6$ ΔG^0_{syn}/kJ=38.2–0.0601 T/K; ΔG^0=0 at 636 K.

The ΔG^0_{syn} values were calculated from the ΔG^0_f equation, where ΔG^0_f (RbCl) and ΔG^o_f (CeCl$_3$) are zero. RbCe$_2$Cl$_7$ is stable at ≥288°C, Rb$_3$CeCl$_6$ at T≥363°C. It should be pointed out, that ΔG^o_{syn} (Rb$_3$CeCl$_6$) is directly measured in an e.m.f. cell RbCl *vs.* 30 mol% CeCl$_3$. Our e.m.f. measurements of Rb- and K-compounds revealed that other systems show the same features as the system RbCl/CeCl$_3$.

Cs-compounds

As already mentioned, there is a change in the coordination number of the Ln^{3+} ions in the compounds CsLn$_2$Cl$_7$ (8→7) when going from Nd to Sm. The CN of Cs$^+$ remains nearly the same in the KEr$_2$Cl$_7$- and RbDy$_2$Cl$_2$-type, with 9/11 and (10+2) well adapted to the large Cs$^+$ ions. For the 2:1-compounds from La to Sm the CN is 8, relatively small, but it becomes higher (10/11) in the Cs$_2$DyCl$_5$-type.

Figure 9 shows that ΔH^0_{syn} for Cs$_2$LaCl$_5$ is rather exothermic, but the heat of reaction gets smaller when going to Cs$_2$NdCl$_5$. The shrinkage of the unit cell with decreasing r(Ln^{3+}) is unfavourable for the eight-coordinated Cs$^+$ ion. On the other hand

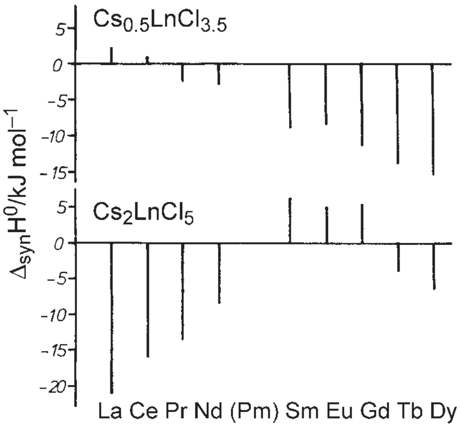


Fig. 9 $\Delta_{syn}H^0$ values for Cs-compounds

Table 8 Results of e.m.f. measurements compared with ΔH_f values from solution calorimetry (ΔG, ΔH in kJ mol^{-1}, ΔS in J K^{-1}mol^{-1})

Rb-compounds	$\Delta G^0_{f\,573}$	ΔH^0_f	ΔS^0_f	$\Delta H^0_{f\,(cal.)}$	K-compounds	$\Delta G^0_{f\,573}$	ΔH^0_f	ΔS^0_f	$\Delta H^0_{f\,(cal.)}$
$Rb_{0.5}LaCl_{3.5}$	-9.5^*	–2.2	12.7	-1.5^*	$K_{0.6}LaCl_{3.6}$	–10.7	–5.3	9.4	–6.8
$Rb_{0.5}CeCl_{3.5}$	–10.9	–2.0	15.5	–1.9	$K_{0.6}CeCl_{3.6}$	–10.1	–4.9	9.1	–5.0
$Rb_{0.5}PrCl_{3.5}$	–13.1	–3.5	16.8	-3.6^*					
$Rb_{0.5}NdCl_{3.5}$	–14.3	–4.8	16.5	–4.3	$K_{0.5}NdCl_{3.5}$	–8.1	1.6	17.0	3.2
$Rb_{0.5}SmCl_{3.5}$	-15.5^*	–14.9	1.0	–14.8	$K_{0.5}SmCl_{3.5}$	-12.3^*	–0.3	21.0	–0.9
$Rb_{0.5}EuCl_{3.5}$	–16.0	–15.4	1.0	–14.2	$K_{0.5}EuCl_{3.5}$	–15.1	–3.2	20.7	–5.2
$Rb_{0.5}GdCl_{3.5}$	(–17.1)	(–16.4)	(1.2)	–16.4	$K_{0.5}GdCl_{3.5}$	(–17.6)	(–9.1)	(14.9)	–9.1
Rb_2LaCl_5	–38.7	–31.4	12.7	–33.3	K_2LaCl_5	–31.2	–22.5	15.1	–24.5
Rb_2CeCl_5	–42.8	–37.4	9.5	–37.9	K_2CeCl_5	–31.1	–29.1	12.0	–27.3
Rb_2PrCl_5	–46.9	–42.8	7.1	–42.7	K_2PrCl_5	–39.1	–31.4	13.4	–34.0
Rb_2NdCl_5	–48.9	–45.7	5.5	–43.3	K_2NdCl_5	-41.8^*	–35.0	11.9	–33.0
Rb_2SmCl_5	-51.0^*	–55.6	–8.0	–55.8	K_2SmCl_5	–47.8	–41.8	10.5	–41.2
Rb_2EuCl_5	–53.0	–60.9	–13.7	–61.1	K_2EuCl_5	–46.9	–44.3	9.7	–43.4
Rb_2GdCl_5	–49.9	–53.4	–6.1	–53.7	K_2GdCl_5	–51.8	–49.7	3.7	–47.8

Table 8 Continued

Rb-compounds	$\Delta G^0_{f\,573}$	ΔH^0_f	ΔS^0_f	$\Delta H^0_{f\,(cal.)}$	K-compounds	$\Delta G^0_{f\,573}$	ΔH^0_f	ΔS^0_f	$\Delta H^0_{f\,(cal.)}$
Rb_3LaCl_6	–28.6*	+16.5	78.8	–					
Rb_3CeCl_6	–39.1	+0.8	69.6	–	K_3CeCl_6	–21.0	24.8	79.9	–
L–Rb_3PrCl_6	–47.6	–16.3	54.7	–	K_3PrCl_6	–26.6	20.5	82.2	–
H–Rb_3PrCl_6	((–46.6))	–7.3	68.6	–					
L–Rb_3NdCl_6	–52.9	–21.6	54.6	–21.9	K_3NdCl_6	–32.2	13.5	79.8	–
H–Rb_3NdCl_6	((–51.8))	–13.6	66.7	–					
L–Rb_3SmCl_6	–62.8*	–41.1	37.9	–40.3	L–K_3SmCl_6	–46.0	–11.2	60.7	–14.5
H–Rb_3SmCl_6	((–60.8*))	–32.9	48.7	–	H–K_3SmCl_6	((–45.5))	–3.2	73.9	–
L–Rb_3EuCl_6	–68.2	–51.2	29.6	–47.6	L–K_3EuCl_6	–51.2	–17.6	58.7	–20.2
H–Rb_3EuCl_6	((–66.9))	–42.7	42.2	–	H–K_3EuCl_6	((–50.4))	–8.9	72.5	–
L–Rb_3GdCl_6	–67.3	–46.7	36.0	–49.6	L–K_3GdCl_6	–55.7	–26.3	51.3	–29.2
H–Rb_3GdCl_6	–	–	–	–	H–K_3GdCl_6	((–54.8))	–17.4	65.3	–
Na-compounds					Na-compounds				
$Na_{0.6}NdCl_{3.6}$	–2.5	5.9	14.7	6.5	Na_2SmCl_5	–5.9	16.0	38.2	14.4
$Na_{0.6}PrCl_{3.6}$	–2.7*	6.9	16.7	6.0	Na_2EuCl_5	–11.1	10.5	37.7	10.7
$Na_{0.6}SmCl_{3.6}$	–2.4	6.1	14.9	4.7	Na_2GdCl_5	–11.6	6.6	31.8	8.8
L–$NaEuCl_4$	–5.2	5.1	17.9	5.0	Na_3EuCl_6	–7.3	24.6	55.6	–
H–$NaEuCl_4$	((–4.8))	10.7	27.1	2.0	H–Na_3GdCl_6	–12.4	17.9	53.9	–
H/L–$NaGdCl_4$	‘–7.5’	‘7.4’	‘26.0’	5.4	L–Na_3GdCl_6 (metastable)	—	–	–	11.2

*values from the original papers corrected by new measurements

( ) e.m.f. measured at one temperature; entropy calculated using $\Delta H^0_{f\,(cal.)}$

(( )) $\Delta G^0_{f\,573}$ values of 573 K metastable states

‘’ formation from NaCl+$GdCl_3$. A phase $Na_{0.5}GdCl_{3.5}$, stable >393°C is not considered

$CsLa_2Cl_7$ is with ΔH^0_{syn}=+1.6 kJ mol^{-1} less stable than its neighbours. With a well-fitting CN ~11 of Cs^+ and CN 8→7 of the Ln^{3+} the synproportionation enthalpies become distinctly exothermic. On the other hand, in Cs_2SmCl_5 CN=6 is still too small for Sm^{3+} ion, but the situation improves with decreasing $r(Ln^{3+})$, and for Tb and Dy the ΔH^0_{syn} are again exothermic.

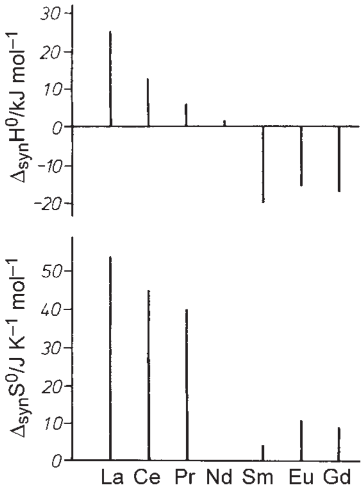


Fig. 10 Enthalpies and entropies for the reactions $CsCl+Cs_2LnCl_5=Cs_3LnCl_6$ [68]

In the meantime, we succeeded in measuring e.m.f. values for the reaction $CsCl+Cs_2LnCl_5=Cs_3LnCl_6$, using improved Cs-conducting diaphragms [45]. The derived ΔG^0_r values are identical with the free synproportionation enthalpies ΔG^0_{syn} (Cs_3LnCl_6). All these compounds with isolated octahedra are formed in their systems from the compounds CsCl and Cs_2LnCl_5 both with linked polyhedra. From La to Nd Cs_2LnCl_5-compounds contain fourfold-connected octahedra. As Fig. 10 reveals, the formation of the hexachlorolanthanides is accompanied by a positive change in lattice enthalpy, compensated by a considerable gain in entropy. The compounds are not stable at T=0 K, but at temperatures given by the relation $\Delta H^0_s=T\Delta S^0_s$. From Sm to Gd the compounds Cs_2LnCl_5 contain twofold-connected octahedra. Now the gain in entropy is only small and the compounds Cs_3LnCl_6 are formed with a negative change in lattice enthalpy. They are stable down to 0 K. Thus the existence area of the Cs-hexachlorolanthanides is steered by the stability of the Cs_2LnCl_5-compounds!

Rb- and K-compounds

All compounds A_2LnCl_5 with A=Rb and K belong to the K_2PrCl_5-type. As can be seen from Table 8 and Fig. 11 they are formed from both, the binary compounds ($2ACl+LnCl_3$) and from their neighbour compounds with a gain in enthalpy, correlated with shrinkage of the mole volumes. They all are stable at 0 K. When at low temperature only compounds A_2LnCl_5 exist then their formation reaction

$2ACl+LnCl_3=Rb_2LnCl_5$ is identical with the synproportionation. Thus, ΔH_f^0-values are the stability determining quantities. They become more exothermic when passing from La to the lanthanides with smaller radii.

An exception is Rb_2GdCl_5. It is the last existing compound in this series. The analogous compounds with Tb and Dy do not exist. Obviously the radii relations are very much unfavourable for CN 7 for Ln^{3+} and CN 8 for Rb^+, and also for the CN 6 and 11 of the Cs_2DyCl_5-type.

Considering entropies of synproportionation from RbCl and $RbLn_2Cl_7$ one can see that there is an entropy loss of approx. 10 J K^{-1} mol^{-1}. As a result the compounds decompose at sufficiently high temperatures. Thus, we conclude that the compounds A_2LnCl_5 are mostly stable at 0 K, but nevertheless melt incongruently.

Rb- and K-compounds ALn_2Cl_7 reveal the same feature as already described for Cs-compounds. The lanthanides from La^{3+} to Nd^{3+} form the KEr_2F_7-type structures, where CN for Ln^{3+} ions is 8 and for A^+ ions 9/11. The compounds ALn_2Cl_7 with *Ln*=Sm–Gd have $RbDy_2Cl_7$- or KDy_2Cl_7-structure with CN 7 and 10+2. That is, a distinct variation in the surroundings only occurs for Ln^{3+} ions, steered by their decreasing size.

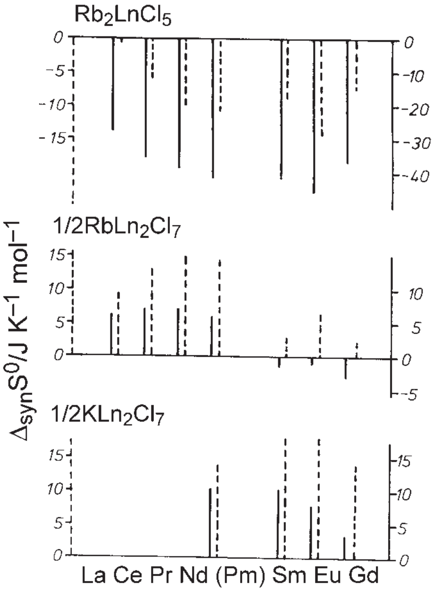


Fig. 11 Synproportionation enthalpies (—) and entropies (---) Rb_2LnCl_5 from RbCl and $RbLn_2Cl_7$; $1/2ALn_2Cl_7$ from A_2LnCl_5 and $LnCl_3$

All compounds with KEr_2Cl_7-structure are formed from their neighbour compounds A_2LnCl_5 and $LnCl_3$ with a positive change in enthalpy. By gain in entropy of 10–15 J K^{-1} mol^{-1} they all exist as high-temperature phases (Fig. 11). For Cs- and Rb-compounds the formation from ACl and $LnCl_3$ is exothermic. For the former the heat of reaction increases with decreasing ionic radii from La (–7 kJ mol^{-1}) to Nd

(–12 kJ mol^{-1}) and is remarkably higher than that for the Rb-compounds. It should be noted that the Cs^+ ions fit better the CN 9/11 against Cl^- than the smaller Rb^+ ions.

With the smaller potassium ion one compound, KNd_2Cl_7, exists with this structure, which is stable only in the small temperature range from 493 to 510°C. It is formed from KCl and $NdCl_3$ with a small positive change of lattice enthalpy, compensated by a gain in entropy of 17 J K^{-1} mol^{-1}. Caused by shrinkage of the $r(Ln^{3+})$ the Cl^- arrangement now fits for the relative small K^+ ion.

For compounds of $RbDy_2Cl_7$ group all ΔH_f^0 values are exothermic. The synproportionation enthalpies are positive for K-compounds, but negative for the compounds $RbSm_2Cl_7$, $RbEu_2Cl_7$ and $RbGd_2Cl_7$. Thus, two groups of compounds are stable at 0 K, namely the group Rb_2LnCl_5 (*Ln*=Sm, Eu or Gd) and the 1:2-compounds. The conditions for that can be derived from the synproportionation reactions.

1. $1.5RbCl+Rb_{0.5}LnCl_{3.5}=Rb_2LnCl_5$

Stable at 0 K, if $\Delta H_f^0(Rb_2LnCl_5)<\Delta H_f^0(Rb_{0.5}LnCl_{3.5})$

2. $1/4Rb_2LnCl_5+3/4LnCl_3=Rb_{0.5}LnCl_{3.5}$

Stable at 0 K, if $4\Delta H_f^0(Rb_{0.5}LnCl_{3.5})<\Delta H_f^0(Rb_2LnCl_5)$

For instance: $\Delta H_f^0(RbGd_{0.5}Cl_{3.5})=-16.4$ kJ mol^{-1}; $\Delta H_f^0(Rb_2GdCl_5)=-53.4$ kJ mol^{-1}

1. $-53.4<-16.4$, 2. $4\times(-16.4)=-65.6<-53.4$

The compounds A_3LnCl_6 with *A*=Rb or K contain isolated $[LnCl_6]^3$-octahedra like the analogous Cs^+-compounds. The relative lattice enthalpies (formation enthalpies ΔH_f^0 from $3ACl+LnCl_3$) decrease with decreasing $r(Ln^{3+})$ and increasing $r(A^+)$. A CN 6 is too small mainly for the early members of the lanthanide series and the ΔH_f^0 values for Rb_3LaCl_6 and Rb_3CeCl_6 are positive. The same holds for the compounds K_3LnCl_6 with *Ln*=Ce, Pr or Nd, while a lanthanum compound does not exist at all. The synproportionation for these compounds between ACl and A_2LnCl_5-compounds of K_2PrCl_5-type is the same as for Cs-compounds from La to Sm. ΔH_{syn}^0 values are endothermic, all the compounds are stable at temperatures much above 0 K. For instance, Rb_3LaCl_6 is formed from its two neighbours with a positive change of nearly 50 kJ mol^{-1} of lattice enthalpy, which is compensated at 444°C by a gain in entropy of 72 J K^{-1} mol^{-1}. An explanation for this high entropy might be given by the fact, that a compound with isolated, and therefore mobile octahedra, is formed from two compounds with rigidly connected polyhedra.

As pointed out in 'The relations between composition and structure' compounds A_3LnCl_6 have elpasolite-like structures, cubic H-modifications and monoclinic L-modifications. Ln^{3+} ions occupy octahedral interstices, CN for alkali ions is (2×12+1×6) in the cubic structure and in a first approximation 8 in the monoclinic structures. However the compounds Rb_3LnCl_6 with *Ln*=La or Ce and K_3LnCl_6 with *Ln*=La–Nd are formed at such high-temperatures that only H-modifications exist. For other K-compounds the transition occurs at ~360°C, for Rb- and Cs-compounds at 390–410°C. Transition enthalpies and formation enthalpies in the reaction $ACl+Ln_2Cl_5\rightarrow A_3LnCl_6$ are measured for compounds of *Ln* (=La–Nd) by the groups of Gaune-Escard *et al.* [69]. The results were completed by c_p-measurements and partially reinterpretated for the groups Rb_3LnCl_6 [70] and K_3LnCl_6 [71].

$\Delta H^0_{\mathrm{trans}}$ values at the transition temperature of the Cs-compounds are 7.4–7.8 kJ mol^{-1} and of Rb_3PrCl_6 and Rb_3NdCl_6 are 6.6 and 6.7 kJ mol^{-1}, respectively. A value of 8.5 kJ mol^{-1} for Rb_3CeCl_6 at 651 K may be the value for a metastable transition, because this temperature is also the formation temperature ($RbCl+Rb_2CeCl_5= Rb_3CeCl_6$). Metastable transitions (of unknown kinds) ought to have an effect of ~1.0 kJ mol^{-1} measured by the aforementioned authors at 130°C for the compounds Rb_3LnCl_6 (*Ln*=Ce–Nd). In our e.m.f. measurements the transitions appeared as small kinks in the e.m.f. curves which do not give precise enthalpy values. Otherwise, the values for the synproportionation reactions $ACl+A_2LnCl_5=A_3LnCl_6$ at the formation temperatures agree well with those of Gaune-Escard *et al.* In their last papers Gaune-Escard and Rycerz calculated the formation enthalpies of K_3LnCl_6 [71] and Rb_3LnCl_6 [70] with *Ln*=Ce, Pr and Nd in the liquid state at ~1100 K using their own data of c_p, $\Delta H_{\mathrm{trans}}$, ΔH_{form}, ΔH_{fus} and data of solutions enthalpies from literature. They compared these calculated data with experimental values of mixing enthalpies of ACl with $LnCl_3$ melts. An agreement between several sources may serve as a probe for the consistency of the sets of the thermodynamical values. In many cases the agreement was fairly well, but in some cases (i.e. Rb_3LaCl_6) there were big discrepancies. Such discrepancies also exist for fusion enthalpies measured by different groups (Table 2, column IV). Here a critical comprehension, in some cases reinvestigation would be of great value.

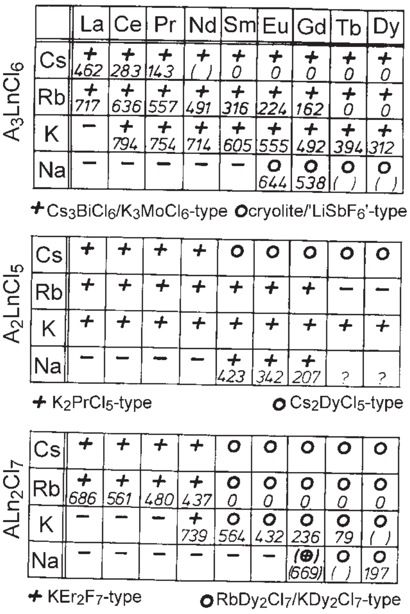
Blachnik and Selle measured solution enthalpies of Cs- and K-compounds A_3LnCl_6 and ALn_2Cl_7 and calculated their formation enthalpies and lattice energies [60]. They found a nearly linear increase of the lattice energy with decreasing radius of the Ln^{3+} ion. That is to be expected from the electrostatic binding model. There is also a correlation between the melting points and the formation enthalpies of these 3:1- and 1:2-compounds [29]. This correlation was explained by Wagner [72] when he treated the correlation between fusion enthalpies and formation enthalpies.

Sodium compounds Na_2LnCl_5 with K_2PrCl_5-structure exist with Sm, Eu and Gd, as explained in 'The relations between composition and structure' using the concept of ionic radii. They are the most stable compounds in their systems, but because of positive formation enthalpies they are not stable at 0 K. Stability ranges of Na_2SmCl_5, Na_2EuCl_5 and Na_2GdCl_5 begin at 323, 242 and 208 K, respectively. These temperatures are calculated from the condition $\Delta G^0_f=0$. These are the temperatures where $T\Delta S\geq\Delta H$. The endothermic enthalpies range from +16.0 to +6.6 kJ mol^{-1} and the entropies from 38.2 to 31.8 J K^{-1} mol^{-1} in Sm- and Gd-compounds, respectively, correlating with the expansion of the mole volumes.

Beginning with europium, also sodium–hexachlorolanthanides exist. According to Meyer they either crystallize in a 'stuffed' $LiSbF_6$-structure [44] or belong to the cryolite-family [43]. These structures are characterized by octahedral coordination of both cations, Na^+ and Ln^{3+}. The lattice enthalpies are positive. That is due to the fact that Eu^{3+} and to some extent also Gd^{3+} are too large to arrange well-fitting octahedra for the sodium ions. The compounds $NaEuCl_4$ and $NaGdCl_4$ where Na^+ and Ln^{3+} occupy interstices in monocapped trigonal prisms [50] still have slightly positive formation enthalpies.

Conclusions

Figure 12 gives a survey on all existing compounds of the three main families, A_3LnCl_6, A_2LnCl_5 and ALn_2Cl_7. In addition, the lowest temperatures of stability are given. The following topics can be seen:



A_3LnCl_6		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
	Cs	+ 462	+ 283	+ 143	+ ( )	+ 0	+ 0	+ 0	+ 0	+ 0
	Rb	+ 717	+ 636	+ 557	+ 491	+ 316	+ 224	+ 162	+ 0	+ 0
	K	–	+ 794	+ 754	+ 714	+ 605	+ 555	+ 492	+ 394	+ 312
	Na	–	–	–	–	–	o 644	o 538	o ( )	o ( )

+ Cs_3BiCl_6/K_3MoCl_6-type o cryolite/'$LiSbF_6$'-type

A_2LnCl_5										
	Cs	+	+	+	+	o	o	o	o	o
	Rb	+	+	+	+	+	+	+	–	–
	K	+	+	+	+	+	+	+	+	+
	Na	–	–	–	–	+ 423	+ 342	+ 207	?	?

+ K_2PrCl_5-type o Cs_2DyCl_5-type

ALn_2Cl_7										
	Cs	+	+	+	+	o	o	o	o	o
	Rb	+ 686	+ 561	+ 480	+ 437	o 0	o 0	o 0	o 0	o 0
	K	–	–	–	+ 739	o 564	o 432	o 236	o 79	o ( )
	Na	–	–	–	–	–	–	(⊕) (669)	o ( )	o 197

+ KEr_2F_7-type o $RbDy_2Cl_7$/KDy_2Cl_7-type

Fig. 12 Ternary lanthanide chlorides with the lowest temperatures (K) of stability

a) All compounds with the composition A_2LnCl_5 are stable at 0 K. Therefore, their stability is given by the lattice enthalpies. That is, the coordination number of Ln^{3+} ions (7 in the K_2PrCl_5-type and 6 in the group with Ln=Sm, Eu, Gd) and of the A^+ ions (8 in the first group, 10/11 in the second) must be favorable.

b) The compounds with the composition ALn_2Cl_7 are stable at 0 K, if they crystallize in the $RbDy_2Cl_7$-type lattice with Ln^{3+} and A^+ ions having CN 7 and 10+2, respectively, provided that the alkali metal ions are large enough. This holds for Cs- and Rb-compounds, but not for K-compounds. K^+ ion seems to be too small for 10+2 coordination, so that its compounds are stable only at temperatures at which the entropy term $T\Delta S$ compensates the positive change in enthalpy. The same consideration is valid for the compounds $RbLn_2Cl_7$ (Ln=La–Sm) which crystallize with the KEr_2F_7-structure with Ln^{3+} and A^+ ions having CN 8 and 9/11, respectively, whereas Cs-compounds have negative synproportionation enthalpies and are stable at 0 K.

c) All compounds with the composition A_3LnCl_6 have isolated $[LnCl_6]$-octahedra. CN of A^+ ions is 12 in the high-temperature modifications (elpasolite type) and ~10 in the low-temperature phases. Only Cs-compounds with smaller Ln^{3+}-ions, beginning with Nd^{3+}, are stable at 0 K. All the other compounds exist owing to a gain in entropy.

As this comprehension reveals, the gain in entropy for the synproportionation and the formation from nACl+$LnCl_3$ can be of dominant importance. For the last reaction type the maximum formation entropy is in general not greater than 20 J K^{-1} mol^{-1}. However, the synproportionation entropies of the compounds A_3LnCl_6 are remarkably higher by 30–80 J K^{-1} mol^{-1}. That ought to be correlated with the fact, that compounds with isolated polyhedra are formed from compounds with associated polyhedra. It should be of great interest, if this topic was treated by means of statistical thermodynamics.

Another group of compounds with the composition $A_3Ln_5Cl_{18}$, is also stabilized by an entropy gain which can be explained by a statistical model. These compounds have three A^+ ions statistically distributed over 1/6 of the Ln^{3+}-sites and 2/3 voids in the lattice. Unclear is the entropy gain of ~25 J K^{-1} mol^{-1} for the compounds $NaEuCl_4$ and $NaGdCl_4$, where a CN 7 was found for Ln^{3+} and for A^+ ions.

To learn more about this entropy effect it is necessary to measure c_p-values down to 0 K. Then the 'production of entropy' can be discovered by integration, and additionally the validity of the extrapolation of enthalpy values, which was used to predict the existence of phases at 0 K, can be confirmed. We have measured c_p-values for the ternary lanthanum chlorides [73] in the temperature range from 200 to 770 K and have found, that $\Delta c_p = c_p(A_nLnCl_{n+3}) - \{nc_p(ACl) + c_p(LnCl_3)\} = 0$, which is the condition of temperature independent ΔH and ΔS. Thus, the following final conclusion can be drawn: Ternary chlorides of the lanthanides exist at 0 K, if the coordination number of Ln^{3+} ions and A^+ ions are so favourable, that the synproportionation from their neighbour compounds in the phase diagram produces a negative change in lattice enthalpy. High-temperature compounds exist, when a sufficiently high gain in entropy exists.

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