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PROPERTIES OF DOUBLE CHLORIDES IN THE SYSTEMS $ACl/NdCl_3$ (A´Na–Cs)

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The pseudobinary systems $ACl/NdCl_3$ (A = Na–Cs) were reinvestigated by means of DTA. The following double chlorides were found primarily detected compounds are underlined): $\underline{Na_3Nd_5Cl_{18}}$; K_3NdCl_6, K_2NdCl_5, $\underline{KNd_2Cl_7}$; $\underline{Rb_3NdCl_6}$, Rb_2NdCl_5, $\underline{RbNd_2Cl_7}$; Cs_3NdCl_6, $\underline{Cs_2NdCl_5}$, $\underline{CsNd_2Cl_7}$.

With a galvanic cell for solid electrolytes the thermodynamic functions of formation from ACl and $NdCl_3$ together with the free enthalpies of synproportionation from the compounds adjacent in the phase diagrams were measured. They revealed, that only the compounds A_2NdCl_5 are stable at ambient temperature. All other compounds are existing by a gain of entropy only at higher temperatures.

The crystal structures of the compounds were determined by X-ray analysis on powders: the compounds are isotypic with the analogous double chlorides of La and Ce (A_3NdCl_6: high-temperature-modification = elpasolite-type; at room-temperature = metastable K_3MoCl_6-type; $A_2NdCl_5 = K_2PrCl_5$-type; $ANd_2Cl_7 = \beta$-KEr_2F_7-type; $Na_3Nd_5Cl_{18} = Na_3La_5Cl_{18}$-type). Magnetic susceptibilities in the range from 80 to 300 K were measured with a Gouy-balance.

In continuation of our research work on phase diagrams of pseudobinary systems $ACl/LnCl_3$ (A = Na–Cs; Ln = La [1], Ce [2], Pr [3], now we have investigated the systems $ACl/NdCl_3$. The phase diagrams were elucidated by means of 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. Additionally, their magnetic properties and crystal structures were measured.

Experimental

$NdCl_3$ was prepared by dehydration of $NdCl_3 \cdot 6H_2O$, yielded by dissolution of Nd_2O_3 (Fa. Ventron, 99.999%) in hydrochloric acid, in an HCl-stream. In the same way the alkali metal chlorides were dried at 500°.

The DTA-measurements were performed in a home-built device for samples (0.5 g) in vacuum-sealed quartz ampoules. Generally heating curves were measured (heating rate: 2 $deg \cdot min^{-1}$).

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The apparatus used for solution calorimetry was a home-built isoperibolic calorimeter. From the enthalpies of solution, ΔH^{l}, the reaction enthalpies, ΔH^{r}, were calculated:

$$\Delta H^{r}_{298} = \{\Delta H^{l}_{298}(\mathrm{NdCl_3}) + n\Delta H^{l}_{298}(\mathrm{ACl})\} - \Delta H^{l}_{298}(A_n\mathrm{NdCl}_{n+3})$$

X-ray-powder patterns: Philips PW 1050/25 goniometer. — High-temperature photos: Simon–Guinier method.

Magnetic measurements: Gouy method at several temperatures in the range from -200 to 100°. Calibration with $\mathrm{HgCo(SCN)_4}$: $x_g = 16.515 \cdot 10^{-6}\ \mathrm{cm^3 \cdot g^{-1}}$ at 18.5°. E.m.f.-measurements: A description of the galvanic cell is given elsewhere [4]. For the formation of the $\mathrm{NdCl_3}$-richest compounds the set-up of the cell was

$$(\mathrm{C}+\mathrm{Cl_2})/\mathrm{ACl}/\mathrm{A}^{+}\text{-conducting diaphragm}/\mathrm{NdCl_3}(+A_n\mathrm{NdCl}_{n+3})/(\mathrm{C}+\mathrm{Cl_2}).$$

The solid electrolytes (compressed disks) were separated by a sintered disk of an A^{+}-conducting glass powder; for Cs^{+} no suitable material could be found yet. The collected e.m.f. *vs.* *T* values were subjected to a linear regression analysis. Temperature range: 300–480°.

Results of the measurements

The phase diagrams

Figure 1 illustrates the results of the DTA investigations. The melting point for $\mathrm{NdCl_3}$ was found at 831°. $\mathrm{Na_3Nd_5Cl_{18}}$ is forming mixed crystals in the temperature range 350–550°. The exact boundaries couldn't be fixed; however, high-temperature X-ray-photos, taken at 450° yielded a range from ~60 to ~75 mol-% $\mathrm{NdCl_3}$: the hexagonal *c*-axis varied from 7.535 to 7.505 Å, whilst the *a*-axis remained constant ($a = 4.237$ Å). — Older investigations [5] had yielded a purely eutectic system with a non-monotonous (!) liquidus line near 60 mol-% $\mathrm{NdCl_3}$.

The compounds $\mathrm{K_3NdCl_6}$ and $\mathrm{K_2NdCl_5}$ are already known from other authors [5, 6]; the system $\mathrm{RbCl/NdCl_3}$ was measured for the first time. In the system $\mathrm{CsCl/NdCl_3}$ from older measurements [5, 6] only $\mathrm{Cs_3NdCl_6}$ was known.

Difficulties arose with the compound $\mathrm{Cs_2NdCl_5}$: it was only formed by annealing a sample for one month at 230°, together with a catalytic amount of water. The same behaviour was found for the decomposition of $\mathrm{Rb_3NdCl_6}$ below 217 °C.

Crystal structures and magnetic moments

The results of X-ray measurements on crystal powders, together with the results of Meyer [7] for some compounds $\mathrm{A_2NdCl_5}$, are summarized in Table 1. The

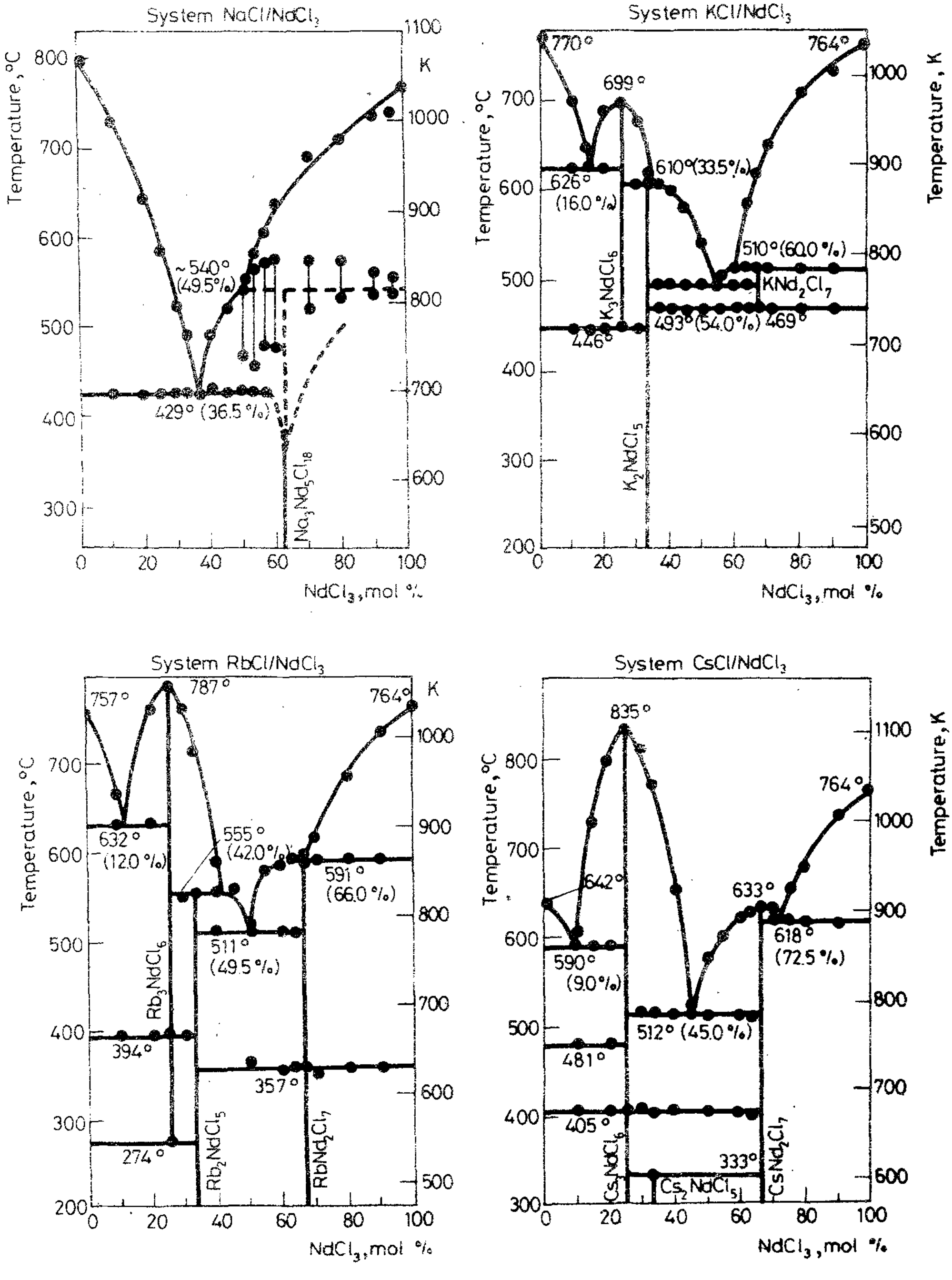

Fig. 1 The systems ACl/NdCl$_3$

Table 1 Unit cell parameters for neodymium double chlorides

Compound	Space group	a/pm	b/pm	c/pm	β/grad
H-Cs_3NdCl_6	Fm3m	1172.8(2)			
D-Cs_3NdCl_6	$P2_1/c$	1405.9(4)	823.6(2)	1328.1(3)	107.68(2)
H-Rb_3NdCl_6	Fm3m	1134.3(2)			
D-Rb_3NdCl_6	$P2_1/c$	1353.4(4)	774.0(3)	1339.8(4)	108.49(2)
K_3NdCl_6	Fm3m	1114.3(1)			
C_2NdCl_5	Pnma	1369.1(3)	910.2(2)	850.9(2)	
Rb_2NdCl_5 [7]	Pnma	1311.1(3)	891.2(2)	817.5(2)	
K_2NdCl_5 [7]	Pnm	1270.7(3)	874.1(3)	796.9(2)	
$CsNd_2Cl_7$	$Pna2_1$	1481.8(9)	1662.7(5)	963.6(3)	
$RbNd_2Cl_7$	$Pna2_1$	1464.4(5)	1674.3(4)	943.0(5)	
KNd_2Cl_7	$Pna2_1$	1445.8(4)	1637.1(8)	972.7(5)	
$Na_3Nd_5Cl_{18}$	$P6_3/m$	753.5(1)		423.7(1)	
$NdCl_3$	$P6_3/m$	739.5(1)		424.1(1)	
$NdCl_3$ [10]	$P6_3/m$	739.6		423.4	

Table 2 Results of magnetic measurements

Compound	Cs_3NdCl_6	Rb_3NdCl_6	Cs_2NdCl_5	Rb_2NdCl_5	K_2NdCl_5
$\mu_{c.w}/\mu_B$	3.73	3.67	3.72	3.62	3.65
$-\theta$/K	30	24	16	11	13
Compound	$CsNd_2Cl_7$	$RbNd_2Cl_7$	KNd_2Cl_7	$Na_3Nd_5Cl_{18}$	$NdCl_3$
$\mu_{c.w}/\mu_B$	3.71	3.84	3.78	3.87	3.88
$-\theta$/K	22	23	22	27	31

compounds A_3NdCl_6 have high-temperature modifications, crystallizing in the cubic elpasolite type and low-temperature forms with K_3MoCl_6-structure [8]. The double chlorides ANd_2Cl_7 are isotypic to β-KEr_2F_7 [9]; the compound $NaNd_{1.67}Cl_6$ has a hexagonal unit cell which can be generated from the $NdCl_3$-structure [10] by substituting each sixth Nd^{3+} by three Na^+.

For Nd^{3+} ($4f^3$-electrons in ${}^4I_{9/12} \rightarrow g = 8/11$) a magnetic moment $\mu_{eff} = g \cdot \sqrt{J'(J+1)} \cdot \mu_B = 3.62\,\mu_B$ is to be expected; the literature value for $NdCl_3$ [11] is 3.78 μ_B, calculated with the Curie-Weiss-law ($\chi_{mol} = C/(T-\theta)$) with $\theta = -31$ K. The own measurements yielded values (Table 2) ranging from 3.6 to 3.9 μ_B with $\theta \sim -25$ K.

Solution calorimetry and e.m.f.-measurements

The solution enthalpy for $NdCl_3$ was found to be $-149.5(4)\ kJ \cdot mol^{-1}$. (Literature: -147.7 to $-153.3\ kJ \cdot mol^{-1}$). The enthalpies for dissolving the alkaline chlorides in $NdCl_3$-solution are ($kJ \cdot mol^{-1}$): $CsCl = 18.1(2)$; $RbCl = 17.6(2)$; $KCl = 17.9(1)$; $NaCl = 4.5(1)$. The results for those compounds, which could be prepared without decomposition products at room temperature together with enthalpies of synproportionation are compiled in Table 3.

Table 3 Solution enthalpies ΔH^1 and related enthalpy values, $kJ \cdot mol^{-1}$

Compound	ΔH^l_{298}	ΔH^f_{298}	ΔH^s_{298}	Synprop. from
Cs_3NdCl_6	$-56.3(6)$	-38.9	$+1.6$	$CsCl$, Cs_2NdCl_5
Cs_3NdCl_6 [12]	-54.3	-39.9	—	
Cs_2NdCl_5	$-72.8(7)$	-40.5	-28.1	$CsCl$, $Cs_{0.5}NdCl_{3.5}$
1/2 $CsNd_2Cl_7$	$-128.1(5)$	-12.4	-2.2	Cs_2NdCl_5, $NdCl_3$
Rb_3NdCl_6	$-74.8(8)$	-21.9	$+21.4$	$RbCl$, Rb_2NdCl_5
Rb_2NdCl_5	$-71.0(3)$	-43.3	-39.0	$RbCl$, $Rb_{0.5}NdCl_{3.5}$
1/2 $RbNd_2Cl_7$	$-136.4(4)$	-4.3	$+6.5$	Rb_2NdCl_5, $NdCl_3$
K_2NdCl_5	$-80.7(3)$	-33.0	-33.0	$KCl/NdCl_3$
1/2 KNd_2Cl_7	$-143.7(2)$	$+3.2$	$+11.5$	K_2NdCl_5, $NdCl_3$
1/5 $Na_3Nd_5Cl_{18}$	$-153.3(6)$	$+6.5$	$+6.5$	$NaCl/NdCl_3$

ΔH^f = reaction enthalpies from $ACl + NdCl_3$; ΔH^s = Synproportionation enthalpies from the neighbour compounds, stable at 298 K.

The e.m.f. values were measured for the formation of the compounds from ACl (with A = K, Rb) and neighbouring compounds richer in $NdCl_3$. (For K_2NdCl_5 only the formation from $NdCl_3$ was measured, because KNd_2Cl_7 is stable only in a small temperature range from 469 to 493°.) The regression line was transformed to the Gibbs–Helmholtz-equation $\Delta G^r = \Delta H^r - T \cdot \Delta S^r$ by multiplication with $-n \cdot F$. By means of thermodynamic cycles, these functions were transformed to those for the reactions $nACl + NdCl_3 = A_nNdCl_{n+3}$, denoted as ΔG^f, ΔH^f and ΔS^f. In Table 4 the energy values ΔG^f_{298}, ΔH^f_{298} and $-(T \cdot \Delta S^f)_{298}$ are compiled in the first three columns. The free enthalpies of synproportionation ΔG^s in the fifth column are calculated for the same reactions as in Table 3. For high-temperature modifications the temperatures of decomposition were calculated by the condition $\Delta G^s = 0 \rightarrow \Delta H^s = T \cdot \Delta S^s$

$\underline{Rb_{0.5}NdCl_{3.5}}$: Reaction $0.5RbCl + NdCl_3 = Rb_{0.5}NdCl_{3.5}$ $\quad n = 0.5$
e.m.f., $mV = 99.46 + 0.3413 \cdot T$, K; $\Delta G^r = \Delta G^f$, $kJ \cdot mol^{-1} = -4.8 - 0.0165 \cdot T$, K

Table 4 Energies of the formation from ACl and $NdCl_3$ at 298 K and free enthalpies of synproportionation ΔG^s_{298} [kJ · mol^{-1}]

Compound	ΔG^f	ΔH^f	$-(T \cdot \Delta S^f)$	$\Delta H^f_{(calorim.)}$	ΔG^s	$\Delta G^s = 0$ at T, K
$Rb_{0.5}NdCl_{3.5}$	− 9.7	− 4.8	− 4.9	− 4.3	+ 1.8	415 (142 °C)
Rb_2NdCl_5	−47.3	−45.7	− 1.6	−43.3	−37.6	—
H–Rb_3NdCl_6	−33.5	−13.6**	−19.9	—	+13.9	664 (391 °C)*
D–Rb_3NdCl_6	−37.9	−21.6**	−16.3	−21.9	+ 9.5	490 (217 °C)
$K_{0.5}NdCl_{3.5}$	− 3.5	+ 1.6	− 5.1	+ 3.2	+ 6.5	732 (459 °C)
K_2NdCl_5	−38.5	−35.0	− 3.5	−33.0	id. ΔG^f	—
K_3NdCl_6	−10.3	+13.5	−23.8	—	+28.3	714 (441 °C)
$Na_{0.6}NdCl_{3.6}$	+ 1.5	+ 5.9	− 4.4	+ 6.5	id. ΔG^f	401 (128 °C)

* Transition temperature H–Rb_3NdCl_6 → D–Rb_3NdCl_6; ** Transition enthalpy: 8.0 kJ · mol^{-1}.

$\underline{Rb_2NdCl_5}$; Reaction $1.5RbCl + Rb_{0.5}NdCl_{3.5} = Rb_2NdCl_5$ $n = 1.5$
e.m.f., mV = $282.57 - 0.0762 \cdot T$, K; ΔG^r, kJ · mol^{-1} = $-40.9 + 0.0110 \cdot T$, K
For $2RbCl + NdCl_3 = Rb_2NdCl_5$: ΔG^f, kJ · mol^{-1} = $-45.7 - 0.0055 \cdot T$, K

$\underline{Rb_3NdCl_6}$: Reaction $RbCl + Rb_2NdCl_5 = Rb_3NdCl_6$ $n = 1$
a) H–Rb_3NdCl_6 (>644 K): e.m.f., mV = $-332.67 + 0.6346 \cdot T$, K; ΔG^r, kJ · mol^{-1} = $32.1 - 0.0612 \cdot T$, K
b) D–Rb_3NdCl_6 (<664 K): e.m.f., mV = $-249.53 + 0.5093 \cdot T$, K; ΔG^r, kJ · mol^{-1} = $24.1 - 0.0491 \cdot T$, K
$\Delta G^r_a = \Delta G^r_b$ at 664 K (391°);
For $3RbCl + NdCl_3$ = D–Rb_3NdCl_6; ΔG^f, kJ · mol^{-1} = $-21.6 - 0.0546 \cdot T$, K

$\underline{K_{0.5}NdCl_{3.5}}$: Reaction $0.5KCL + NdCl_3 = K_{0.5}NdCl_{3.5}$ $n = 0.5$
e.m.f., mV = $-32.54 + 0.3527 \cdot T$, K; $\Delta G^r \equiv \Delta G^f$, kJ · mol^{-1} = $1.6 - 0.0170 \cdot T$, K

$\underline{K_2NdCl_5}$: Reaction $2KCl + NdCl_3 = K_2NdCl_5$ $n = 2$
e.m.f., mV = $181.18 + 0.0615 \cdot T$, K; $\Delta G^r \equiv \Delta G^f$, kJ · mol^{-1} = $-35.0 - 0.0199 \cdot T$, K

$\underline{K_3NdCl_6}$: Reaction $KCl + K_2NdCl_5 = K_3NdCl_6$ $n = 1$
e.m.f., mV = $-502.63 + 0.7035 \cdot T$, K; ΔG^r, kJ · mol^{-1} = $48.5 - 0.0679 \cdot T$, K
For $3KCl + NdCl_3 = K_3NdCl_6$: ΔG^f, kJ · mol^{-1} = $13.5 - 0.0798 \cdot T$, K

$\underline{Na_{0.6}NdCl_{3.6}}$: Reaction $0.6NaCl + NdCl_3 = Na_{0.6}Nd_{3.6}$ $n = 0.6$
e.m.f., mV = $-102.48 + 0.2545 \cdot T$, K; $\Delta G^r \equiv \Delta G^f$, kJ · mol^{-1} = $5.9 - 0.0147 \cdot T$, K.

Conclusions

1. The free enthalpies of synproportionation ΔG^s in Table 4 indicate, that in the systems with KCl and RbCl only the compounds A_2NdCl_5 are stable at ambient temperature. In the system $CsCl/NdCl_3$, the compounds Cs_2NdCl_5 and $CsNd_2Cl_7$ are stable, as can be seen from the enthalpies of synproportionation ΔH^s in Table 3.

2. The compounds ANd_2Cl_7 (A = Rb, K) and A_3NdCl_6 are stable only at high temperatures: a loss of (lattice) enthalpy is compensated by a gain in entropy. In the case of the 3:1-compounds this entropy gain is correlated with the formation of isolated $[NdCl_6]^{3-}$-octahedra.

3. In the system $NaCl/NdCl_3$ a phase $Na_3Nd_5Cl_{18}$ exists, stable > 128°. It can be considered as a solid solution of NaCl in the $NdCl_3$-lattice.

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References

1 H.-J. Seifert, H. Fink and G. Thiel, J. Less-Common Metals, 110 (1985) 159.
2 H.-J. Seifert, J. Sandrock and G. Thiel, J. Thermal Anal., 31 (1987) 1309.
3 H.-J. Seifert, J. Sandrock and J. Uebach. Z. anorg. allg. Chem., in press.
4 H.-J. Seifert, and G. Thiel, J. Chem. Thermodyn., 14 (1982) 1159.
5 R. Förthmann, G. Vogel and A. Schneider, Z. anorg. allg. Chem., 367 (1969) 19.
6 Sun in'-Chzhu and I. S. Morozov, Z. Neorg. Khim., 3 (1958) 1914.
7 G. Meyer and E. Hüttl, Z. anorg. allg. Chem., 497 (1983) 191.
8 Z. Amilius, B. van Laar and H. M. Rietveld, Acta Crystalogr,, B25 (1969) 400.
9 S. Alenoard, Y. Le Für, M. F. Gorius and M. T. Roux, J. Solid State Chem., 34 (1980) 79.
10 W. Zachariasen, J. Chem. Phys., 16 (1948) 254.
11 R. A. Sallach and J. D. Corbett, Inorg. Chem., 3 (1964) 993.
12 R. Blachnik and D. Selle, Z. anorg. allg. Chem., 454 (1979) 82.

Zusammenfassung — Die pseudobinären Systeme $ACl/NdCl_3$ (A = Na–Cs) wurden mittels DTA neu untersucht. Folgende Doppelchloride wurden gefunden (erstmalig beschriebene Verbindungen sind unterstrichen): $\underline{Na_3Nd_5Cl_{18}}$; K_3NdCl_6, K_2NdCl_5, $\underline{KNd_2Cl_7}$; $\underline{Rb_3NdCl_6}$, Rb_2NdCl_5, $\underline{RbNd_2Cl_7}$; Cs_3NdCl_6, $\underline{Cs_2NdCl_5}$, $\underline{CsNd_2Cl_7}$.

Mit einer galvanischen Zelle für feste Elektrolyte wurden die thermodynamischen Funktionen für die Bildung aus ACl und $NdCl_3$ sowie die freien Enthalpien für die Synproportionierung aus den im Zustandsdiagramm benachbarten Verbindungen gemessen. Es zeigte sich, daß nur die Verbindungen A_2NdCl_5 bei Normaltemperaturen stabil sind. Alle anderen Verbindungen existieren aufgrund von Entropiegewinnen nur bei höheren Temperaturen. Anhand von Röntgen-Pulveraufnahmen wurden die

Kristallstrukturen ermittelt. Die Verbindungen sind isotyp zu den entsprechenden Doppelchloriden des Lanthans und Cers (A_3NdCl_6: Hochtemperaturmodifikationen = Elpasolith-Typ; bei Normaltemperatur metastabil im K_3MoCl_6-Typ; $A_2NdCl_5 = K_2PrCl_5$-Typ; $ANd_2Cl_7 = \beta$-KEr_2F_7-Typ; $Na_3Nd_5Cl_{18} = Na_3La_5Cl_{18}$-Typ). Mit einer Gouy-Waage wurden die magnetischen Suszeptibilitäten im Temperaturbereich 80–300 K gemessen.

Резюме — Методом ДТА вновь исследованы псевдобинарные системы $ACl/NdCl_3$, где A = Na—Cs. Были найдены следующие двойные соли хлоридов, из которых впервые обнаруженные соединения подчеркнуты: $Na_3Nd_5Cl_{18}$, K_3NdCl_6, K_2NdCl_5, KNd_2Cl_7, Rb_3NdCl_6, Rb_2NdCl_5, $RbNd_2Cl_7$, Cs_3NdCl_6, Cs_2NdCl_5, $CsNd_2Cl_7$. С помощью гальванической ячейки на основе твердых электролитов были определены термодинамические функции образования солей, наряду со свободными энтальпиями синпропорционирования из смежных соединений на фазовых диаграммах. Они показали, что при обычной температуре устойчивы только соединения состава A_2NdCl_5. Все остальные соединения с увеличенной энтропией существуют только при более высоких температурах. Кристаллические структуры соединений были определены с помощью порошкового рентгенофазового анализа. Установлено, что все соединения изоморфны с аналогичными двойными хлоридами лантана и церия. Высокотемпературная модификация соединения A_3NdCl_6 является типом елпасолита, а комнатнотемпературная модификация — типом метастабильной K_3MoCl_6. Соединения A_2NdCl_5 — типа K_2PrCl_5, ANd_2Cl_7 — типа β-KEr_2F_7, $Na_3Nd_5Cl_{18}$ — типа $Na_3La_5Cl_{18}$. Методом Гуи в области температур 80—300 К были измерены магнитные восприимчивости.