

# MELTING POINTS OF LANTHANIDE TRICHLORIDES

## An unsolved problem

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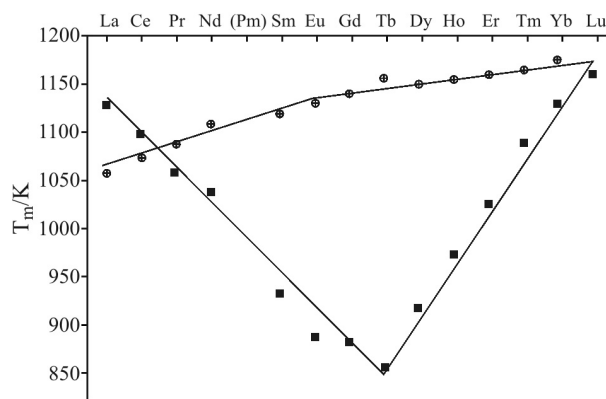
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The melting temperatures and absolute values of melting enthalpies of lanthanide trichlorides decrease from  $\text{LaCl}_3$  to  $\text{TbCl}_3$  and then increase to  $\text{LuCl}_3$ . The preceding decrease cannot be explained by the lattice energies of the trichlorides, since they increase continuously from the lanthanum to the lutetium compounds. However, it may be attributed to the structural features of the liquid state. The liquids near the melting points consist of clusters of complex units, which become larger with decreasing radii of the metal ions. To prove this assumption additional quantitative investigations are necessary.

**Keywords:** lanthanide trichlorides, lattice energies, melting-enthalpies, melting-temperatures, structures of  $\text{LnCl}_3$ -melts

### Introduction

The melting points of the trichlorides of the lanthanide elements decrease from  $\text{LaCl}_3$  to  $\text{TbCl}_3$  and then rise from  $\text{DyCl}_3$  to  $\text{LuCl}_3$  (Fig. 1). The same phenomenon exists with their melting enthalpies  $\Delta H_m^\circ$  (Fig. 2). On the other hand we found in connection with our investigations of the phase diagrams  $\text{ACl/LnCl}_3$  ( $A=\text{Na}-\text{Cs}$ ) that the compounds  $\text{Cs}_3\text{LnCl}_6$ , consisting of  $[\text{LnCl}_6]^{3-}$  and  $\text{Cs}^+$  ions, exhibit a ‘normal behaviour’, namely their melting points rise with decreasing ionic radii of the lanthanides (as their absolute lattice energies increase) from  $\text{Cs}_3\text{LaCl}_6$  (1053 K) to  $\text{Cs}_3\text{TbCl}_6$  (1153 K), and then slowly further to  $\text{Cs}_3\text{YbCl}_6$  (1171 K), with the exception of  $\text{Cs}_3\text{DyCl}_6$  (1148 K). A convincing explanation for the ‘anomalous behaviour’ of the binary chlorides has not been given until now.

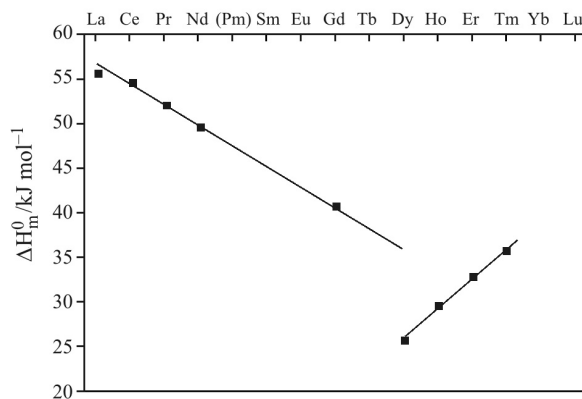


**Fig. 1** Melting temperatures in K of  $\text{LnCl}_3$  and  $\text{Cs}_3\text{LnCl}_6$  compounds ■ – binary chlorides; ● – ternary chlorides  $\text{Cs}_3\text{LnCl}_6$

### Thermal and thermodynamic properties of $\text{LnCl}_3$ compounds

The melting temperatures in Table 1 are mean values taken from our own investigations of phase diagrams of  $\text{ACl/LnCl}_3$  [1, 2] and from Gaune-Escard *et al.* [3]. The melting enthalpies were either measured by Dworkin and Bredig [4, 5] or by Gaune-Escard *et al.* [3]. The former were determined by drop-calorimetry (melt→ambient temperature) and the latter were measured up to 1100 K with DSC (differential scanning calorimetry) or with a high-temperature Calvet microcalorimeter ( $\text{LaCl}_3$ ,  $\text{TmCl}_3$ ). The maximum differences between the results of the two groups are  $2 \text{ kJ mol}^{-1}$ .

The melting entropies  $\Delta S_m^\circ = \Delta H_m^\circ / T$  form two groups. From  $\text{CeCl}_3$  to  $\text{GdCl}_3$  they lie between 45 and  $50 \text{ J K}^{-1} \text{ mol}^{-1}$  and beginning with  $\text{DyCl}_3$  they are be-



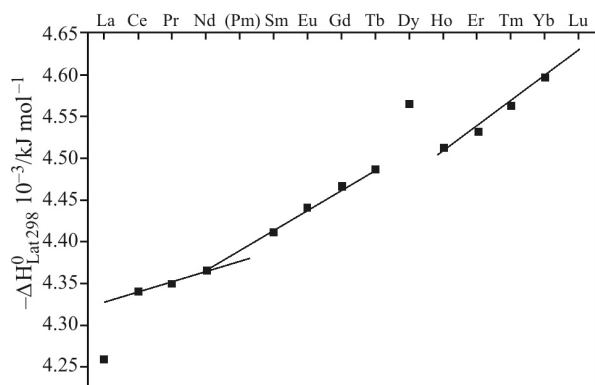
**Fig. 2** Melting enthalpies  $\Delta H_m^\circ$  in  $\text{kJ mol}^{-1}$  of  $\text{LnCl}_3$  compounds

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**Table 1** Thermodynamic properties of lanthanide trichlorides (all energies in kJ mol<sup>-1</sup>)

|                   | I       | II                 | III                | IV                   | V                      | VI    |
|-------------------|---------|--------------------|--------------------|----------------------|------------------------|-------|
|                   | $T_m/K$ | $\Delta H_m^\circ$ | $\Delta H_f^\circ$ | $\Sigma I + E_{sub}$ | $\Delta H_{lat}^\circ$ | MAPLE |
| LaCl <sub>3</sub> | 1126    | 55.7               | -1072              | 3887                 | -4260                  | -4365 |
| CeCl <sub>3</sub> | 1098    | 54.5               | -1060              | 3978                 | -4339                  | -4297 |
| PrCl <sub>3</sub> | 1060    | 52.1               | -1059              | 3991                 | -4351                  | -4415 |
| NdCl <sub>3</sub> | 1032    | 49.2               | -1042              | 4022                 | -4365                  | -4436 |
| SmCl <sub>3</sub> | 941     |                    | -1026              | 4083                 | -4410                  |       |
| EuCl <sub>3</sub> | 895     |                    | -936               | 4192                 | -4429                  | -4485 |
| GdCl <sub>3</sub> | 880     | 40.6               | -1018              | 4145                 | -4464                  | -4496 |
| TbCl <sub>3</sub> | 855     |                    | -1010              | 4158                 | -4469                  | -4454 |
| DyCl <sub>3</sub> | 921     | 25.5               | -994               | 4288                 | -4583                  | -4464 |
| HoCl <sub>3</sub> | 973     | 29.3               | -998               | 4210                 | -4509                  |       |
| ErCl <sub>3</sub> | 1024    | 32.6               | -995               | 4233                 | -4529                  |       |
| TmCl <sub>3</sub> | 1094    | 35.6               | -996               | 4254                 | -4551                  |       |
| YbCl <sub>3</sub> | 1135    |                    | -960               | 4334                 | -4595                  |       |
| LuCl <sub>3</sub> | 1174    |                    | -987               | 4426                 | -4714                  |       |

tween 27 and 32 J K<sup>-1</sup> mol<sup>-1</sup>. The compounds of the first group crystallize in the three dimensional coordination lattice of the UCl<sub>3</sub>-type [6], the coordination number (CN) of the Ln<sup>3+</sup> ions vs. the Cl<sup>-</sup> ions is 9. TbCl<sub>3</sub> is trimorphic [7]. Beginning with the high-temperature modification of the dimorphic DyCl<sub>3</sub> the compounds have a layer-structure of the YCl<sub>3</sub>-type [8] with a CN of Ln<sup>3+</sup> of only 6. The transition from a higher ordered three-dimensional lattice to a layer lattice is associated with a gain in entropy. This can be seen at the transition from the three-dimensional lattice of L-DyCl<sub>3</sub> to H-DyCl<sub>3</sub> at 342°C. The melting enthalpy of 25.5 kJ mol<sup>-1</sup> lies in Fig. 2 as the lowest one on the line of the AlCl<sub>3</sub>-type compounds. When adding the transition enthalpy of 9.3 kJ mol<sup>-1</sup>, measured by us with DSC [9], a value of 34.8 kJ mol<sup>-1</sup> results, which lies near the line for the UCl<sub>3</sub>-type compounds. The transition entropy is 15.1 J K<sup>-1</sup> mol<sup>-1</sup>.

**Fig. 3** Lattice enthalpies [ $-\Delta H_{lat}^\circ$ ] in  $10^3$  kJ mol<sup>-1</sup> of LnCl<sub>3</sub> compounds

Goryushkin *et al.* [10] also measured a set of melting parameters. However, their temperatures and enthalpies are irregularly higher than those compiled in Table 1. The differences for the compounds of the yttrium subgroup are in general larger than those of the cerium subgroup [11]. As a reason for these discrepancies they pointed to the results of an investigation from 1986 [12], where it was found by DSC and DTG (differential thermogravimetry) that lanthanide trichlorides decomposed when heated to temperatures higher than their critical temperatures, which decrease from LaCl<sub>3</sub> to EuCl<sub>3</sub> (~300°C). Therefore, they performed their measurements in a quasi-chlorine atmosphere by adding CCl<sub>4</sub> to the samples. However, cleavage of chlorine in considerable amounts is reported only for EuCl<sub>3</sub> [13].

A further source of error exists for the trichlorides of the smaller lanthanide ions. They react slowly with the SiO<sub>2</sub> of quartz ampoules. Thus, for ErCl<sub>3</sub> the melting temperature measured in a corundum crucible was found at 751°C. After several melting cycles in quartz crucible the effect splits. After three runs two effects were found, at 743 and 770°C [14]. An analogous reaction of SiO<sub>2</sub> with ScCl<sub>3</sub>, forming Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, was described in 1978 by Polyachenok *et al.* [15].

In column III of Table 1 formation-enthalpies  $\Delta H_f^\circ$ (LnCl<sub>3</sub>) are compiled. They were taken from a recent collection of Cordfunke *et al.* [16]. They become less negative from LaCl<sub>3</sub> (-1072 kJ mol<sup>-1</sup>) to TbCl<sub>3</sub> (-1010 kJ mol<sup>-1</sup>), and are nearly constant (~995 kJ mol<sup>-1</sup>) from DyCl<sub>3</sub> to LuCl<sub>3</sub>, again with strong deviations for EuCl<sub>3</sub> and YbCl<sub>3</sub>. For the enthalpy values of the YCl<sub>3</sub>-type compounds another source of errors in their solution enthalpies should be taken into

account. If these layer-structure chlorides crystallize too rapidly, for instance by quenching from the melt or from the gaseous state, or when dehydrating hydrates in a HCl stream at too low temperatures, highly distorted phases are obtained. We found for a DyCl<sub>3</sub> quenched from the melt a solution enthalpy of  $-205.0 \text{ kJ mol}^{-1}$  instead of  $-197.1 \text{ kJ mol}^{-1}$  for the PuBr<sub>3</sub>-type, the stable modification at ambient temperature, while the solution enthalpy of a metastable modification with the YCl<sub>3</sub>-structure is  $-210.2 \text{ kJ mol}^{-1}$  [9].

To conclude, it is necessary to redetermine thermodynamic data of the lanthanide chlorides, namely, the formation enthalpies of the chlorides with the layer structure, and the melting enthalpies, where the deviations of the results of Goryushkin are large.

### Lattice energies

If LnCl<sub>3</sub> melts would consist of isolated ions then lattice enthalpies  $\Delta H_{\text{lat}}^{\circ}(\text{LnCl}_3)$  were of great importance. We have calculated these 'formation -enthalpies' from the gaseous ensemble ( $\text{Ln}_{\text{g}}^{3+} + 3\text{Cl}_{\text{g}}^{-}$ ) with the Born-Haber cycle.

$$\Delta H_{\text{lat}}^{\circ}(\text{LnCl}_3) = \Delta H_{\text{sub}}^{\circ}(\text{Ln}) + 1.5E_{\text{diss}}(\text{Cl}_2) - \Delta H_{f,298}^{\circ}(\text{LnCl}_3) + \left\{ \sum I(\text{Ln}) + 3E_{\text{A}}(\text{Cl}) \right\}$$

Sublimation enthalpies of the metals,  $\Delta H_{\text{sub},298}^{\circ}(\text{Ln})$ , were taken from a paper of Nugent, Burnett and Morss [17]. They are in good agreement with the results of later measurements, the most recent by Zaitzev *et al.* [18] determined with the Knudsen technique. The dissociation energy  $E_{\text{diss}}(\text{Cl}_2) = +244 \text{ kJ mol}^{-1}$  and the electron affinity  $E_{\text{A}}(\text{Cl}) = -355 \text{ kJ mol}^{-1}$  were taken from modern textbooks of inorganic chemistry.

The highest terms in the Born-Haber cycles are the ionisation potentials, namely, the energies for  $\text{Ln}_{(\text{g})} \rightarrow \text{Ln}_{(\text{g})}^{3+} + 3\text{e}^{-}$ . While for all lanthanide metals the first and second ionisation energies are known from spectroscopic measurements, the third potentials were only measured for La, Ce, Pr, Ho and Yb. With these values Johnson [19] and independently Faktor and Hanks [20] calculated lattice energies for their metal oxides and estimated them for the remaining oxides with a function for the lattice parameters. The values of  $\sum I + E_{\text{sub}}$  appearing in column IV in Table 1 are based on the above explained procedure, applying more recent values of formation enthalpies of the oxides taken from a collection of Cordfunke [21]. They agree within  $\sim 1\%$  with data given by Sugar and Reader [22].

Lattice enthalpies at 298 K were calculated from the above-described terms and are collected in column V of Table 1. The energy gain for the hypothetical re-

action  $\text{Ln}_{(\text{g})}^{3+} + 3\text{Cl}_{(\text{g})}^{-} \rightarrow \text{LnCl}_{3(\text{s})}$  increases from LaCl<sub>3</sub> ( $4.20 \cdot 10^3 \text{ kJ mol}^{-1}$ ) to LuCl<sub>3</sub> ( $4.71 \cdot 10^3 \text{ kJ mol}^{-1}$ ) with DyCl<sub>3</sub> as the only exception. This behaviour is expected, because with decreasing  $r(\text{Ln}^{3+})$  and consequently decreasing volumes of the unit cells the Madelung part of the lattice energy (MAPLE) increases. MAPLE values, calculated by Prof. Hoppe from the University of Giessen, (column VI) support this assertion. However, it must be pointed out that for the YCl<sub>3</sub>-type compounds MAPLE values could not be calculated because no atomic parameters (0,y,0) for the Cl<sup>-</sup> are known. A complete structure determination exists only for YCl<sub>3</sub> [8].

To conclude, the anomalous variation of the melting-temperatures and -enthalpies of the lanthanide trichlorides cannot be explained by the variation of their lattice energies, thus it should be attributed to the (structural?) properties of the melts. To the best of our knowledge this idea was at first suggested by Goryushkin in 1996 [23].

### Structure of LnCl<sub>3</sub> melts

Most information about structures of LnCl<sub>3</sub> melts were obtained by investigating molten ACl/LnCl<sub>3</sub> systems, where A is an alkali metal cation. Here the group of Gaune-Escard was dominating.

### Microscopic properties

Papatheodorou [24] found by a systematic examination of Raman-spectra of ACl-YCl<sub>3</sub> liquid mixtures, and especially of the solid and liquid compounds Cs<sub>2</sub>NaYCl<sub>6</sub>, Cs<sub>3</sub>YCl<sub>6</sub> and K<sub>3</sub>YCl<sub>6</sub>, that they all contain  $[\text{YCl}_6]^{3-}$  units. With increasing polarizing power of the cations, that is with decreasing  $r(\text{A}^{+})$ , the Y-Cl bonds are weakened and thus the stability of the complexes diminishes. This effect is still stronger in the binary chloride YCl<sub>3</sub>, where the A<sup>+</sup> ion is substituted by Y<sup>3+</sup>, due to its higher polarizing power. This leads to the presence of Y $\cdots$ Cl $\cdots$ Y interactions instead of isolated  $[\text{YCl}_6]^{3-}$  complexes. In the melt clusters are formed with a quasi-layer-type structure, as it exists in the layers of solid YCl<sub>3</sub>.

These results were confirmed by Adya *et al.* [25] by neutron diffraction studies of molten NdCl<sub>3</sub>, YCl<sub>3</sub> and DyCl<sub>3</sub>. By evaluation with the 'polarizability ion model' (PIM) for DyCl<sub>3</sub> was deduced that molten DyCl<sub>3</sub> has a network structure with corners and edges sharing octahedral  $[\text{DyCl}_6]^{3-}$  units. LaCl<sub>3</sub> has a rather loose ionic-type liquid structure with sixfold coordination of the cations by halogens, as confirmed by X-ray diffraction.

Thus, the following picture results: in melts of lanthanide trichlorides associated  $(\text{LnCl}_3)_x$  units seem to exist which are more or less dissociated according to an equilibrium for the end-states



This equilibrium should be shifted to the right side at sufficiently high temperatures and should lie more at the side of the polymers (left side) the stronger the polarising power of the cation is, i.e., the smaller the lanthanide radius is.

### Macroscopic properties

This conception is supported by measurements of certain macroscopic properties. However, no complete series of measurements exists.

Mochinaga *et al.* [26] measured the molar-volumes ( $V_m$ ) of six liquid lanthanide chlorides as a function of temperature. At 1000 K they are  $73.5 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$  for  $\text{LaCl}_3$ ,  $\text{PrCl}_3$ ,  $\text{NdCl}_3$  and  $75.4 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$  for  $\text{GdCl}_3$ ,  $\text{DyCl}_3$ ,  $\text{YCl}_3$ . These results do not allow any conclusion. However, it is noteworthy to mention that the volume change ( $V_m - V_s$ ), where  $V$  denotes volume and subscripts m and s indicate molten and solid phases, is nearly zero for compounds with a layer structure in the solid state, suggesting similarity of the solid and liquid structures. On the other hand, the chlorides from  $\text{LaCl}_3$  to  $\text{GdCl}_3$  show a large volume increase of  $\sim 20\%$  on melting, which suggests that the distances between these ions increase significantly by fusion, a behaviour similar to that occurring during the fusion of alkali metal chlorides [27].

Evidence for the correctness of the PIM conception is given by measurements of the electric conductivity of  $\text{LnCl}_3$  melts. The most extensive investigations are those of Förthmann and Schneider [28] (Fig. 4). They found that the specific conductivity  $\kappa$  of seven molten lanthanide chlorides, measured at 1073 and 1173 K, decrease linearly with decreasing ionic radii as to be expected from the PIM conception. Their  $\kappa$ -values are in excellent agreement with those of Bredig and Dworkin [29] for  $\text{CeCl}_3$ ,  $\text{PrCl}_3$  and  $\text{NdCl}_3$ , and with deviations of  $\sim 4\%$  with  $\kappa$  values of Mochinaga *et al.* [30] for  $\text{PrCl}_3$  and  $\text{NdCl}_3$ . But there are severe discrepancies with the results of Gaune *et al.* and their interpretations [31].

In conclusion, spectroscopic investigations and measurements of electric conductivities confirm the PIM conception that near the melting temperature melts of lanthanide trichlorides contain clusters consisting of  $(\text{LnCl}_3)_x$ -polymers, the stability of which increases with decreasing radius of the  $\text{Ln}^{3+}$  ion and with increase of its polarizing power [33]. For the

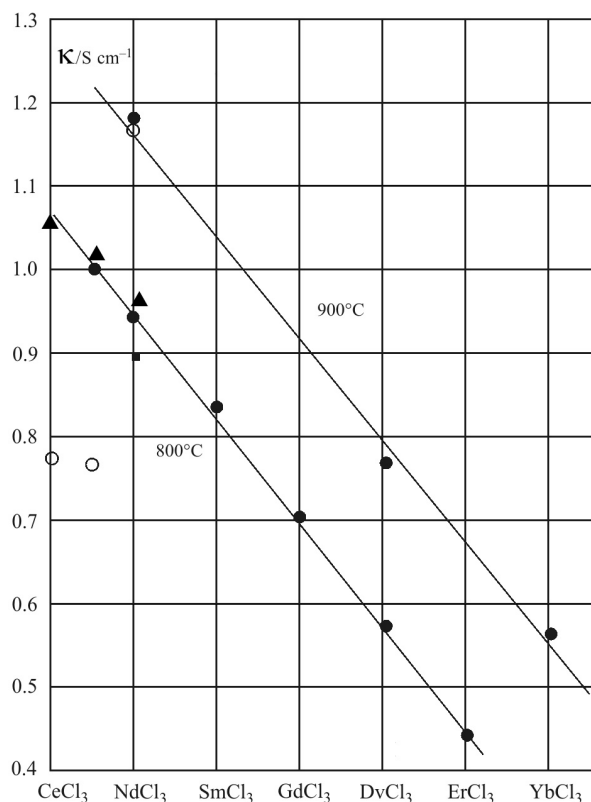


Fig. 4 Electric conductivities  $\kappa$  in  $\text{S cm}^{-1}$  of some  $\text{LnCl}_3$  compounds at 800 and 900°C (● – Förthmann *et al.* [28]; ▲ – Dworkin *et al.* [29]; ■ – Mochinaga *et al.* [30]; ○ – Gaune-Escard *et al.* [34])

completeness of this argument about all lanthanide chlorides, similar measurements must be carried out, mainly with the late members of the lanthanide series.

### Mixing enthalpies in the systems $\text{ACl/LnCl}_3$

Further support for the above conception is given by the results of measurements of mixing enthalpies in systems of the type  $\text{ACl/LnCl}_3$  and especially on pure compounds  $\text{A}_3\text{LnCl}_6$  with the heavier alkali metal ions. First measurements were carried out by Dienstbach and Blachnik [32] ( $\text{GdCl}_3$ ) and Papatheodorou *et al.* [33] ( $\text{LaCl}_3$  and  $\text{CeCl}_3$ ) and were accomplished in 1994-1996 by Gaune-Escard *et al.* [34]. Their last paper [35] from 1998 dealt with the systems  $\text{ACl/TbCl}_3$ .

For all investigated systems with K, Rb and Cs the values of the mixing enthalpies are negative with a minimum of  $\Delta H_{\text{mix}}^{\circ}$  near a composition of 25 mol-%  $\text{LnCl}_3$ . Gaune-Escard *et al.* calculated formation enthalpies  $\Delta H_{\text{f,m}}^{\circ}$  for the reactions  $3\text{ACl}_{(l)} + \text{LnCl}_{3(l)} \rightarrow \text{A}_3\text{LnCl}_{6(l)}$  with  $\text{Ln} = \text{La, Cs, Pr and Nd}$ . For the same alkali metal they differ only in the range of  $\pm 3 \text{ kJ mol}^{-1}$ , and decrease linearly with the ionic radius of  $\text{A}^+$ . Together with the results of the spectro-



scopic and conductivity measurements the authors concluded that with  $A=\text{Cs}$  only  $[\text{LnCl}_6]^{3-}$  complexes (with  $3\text{Cs}^+$  ions) exist in the melt. With decreasing radius of  $A^+$  higher polymers were found, for example,  $2([\text{LnCl}_6]^{3-} + 3A^+) \rightarrow [\text{Ln}_2\text{Cl}_{11}]^{5-} + \text{Cl}^- + 6A^+$ . Thus, the absolute value of the formation enthalpy  $\Delta H_{\text{fm}}^o$  ( $A_3\text{LnCl}_6$ ) becomes smaller, and the electrical conductivity increases by the increasing release of  $\text{Cl}^-$  ions.

It can be shown [1, 2] that all compounds of the type  $A_3\text{LnCl}_6$  crystallize in a wide range of temperatures below their melting points with the cubic elpasolite structure. In this structure type  $[\text{LnCl}_6]^{3-}$  octahedra are held together by the alkali metal ions with the same coordination as in their melts.

Consequently, the melting process of the Cs-compounds  $\text{Cs}_3\text{LnCl}_6$  is controlled by the lattice energy of the solids, and with decreasing lanthanide radius the melting temperature increases, as shown in Fig. 1. For the Rb- and K-compounds the melting points lie at lower temperatures, the melting enthalpies are smaller, though the absolute values of the lattice energies increase with decreasing radii.

### The melting temperatures of the binary chlorides $\text{LnCl}_3$

For the melts of the binary chlorides the existence of isolated  $[\text{LnCl}_6]^{3-}$  ions is improbable because their threefold negative charge must be compensated by free  $\text{Ln}^{3+}$  ions. These ions with polarizing fields stronger than those of the small alkali metal ions enforce the formation of polymeric three-dimensional networks in which they are incorporated. This tendency becomes the stronger the smaller the lanthanide ions are.

With this conception one can divide the melting process into two consecutive steps. First, the solid lattice is broken up to the polymeric three-dimensional networks, a special kind of 'pre-melting'. Secondly, the polymeric units dissociate at elevated temperatures to single ions, what we called in the beginning 'ideal melting'. If the polymerisation energy is more dominant than the lattice energy, the decreasing melting temperature from  $\text{LaCl}_3$  to  $\text{TbCl}_3$  can be explained with increasing polymerisation in the melt. Assuming, that this process is completed with  $\text{TbCl}_3$ , as the cation atomic number increases beyond that of  $\text{DyCl}_3$ , the variation of the lattice energy alone would be directing the melting temperatures, which now increases 'normally' till  $\text{LuCl}_3$ .

It must be pointed out that all these conclusions depend on rather incomplete investigation results. Thus measurements of  $C_p$ -values and of electric conductivities must be extended to those temperatures where 'ideal melts' will exist, and also measurements on the late lanthanides should be performed.

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