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THERMODYNAMIC PROPERTIES OF SOME LANTHANIDE CHLORIDES

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The heat capacities of the lanthanide chlorides $NdCl_2$, $SmCl_2$, $EuCl_2$, $DyCl_2$, $TmCl_2$, $YbCl_2$, $DyCl_3$, $YbCl_3$ and $LuCl_3$ were measured at 10–320 K with an adiabatic microcalorimeter.

Standard thermodynamic properties were calculated from the experimental results.

The heat capacities of these chlorides are composed of the lattice heat capacity and an additional contribution caused by the thermal population of the low-lying Stark electronic levels (Schottky anomaly). The Schottky heat capacity was estimated as the difference between the experimental C_p values for the isostructural paramagnetic and diamagnetic chlorides. Experimental Schottky contributions were found to be in good agreement with those calculated for $SmCl_2$, $TmCl_2$ and $YbCl_3$ via a general model of the main-term Stark splitting of the respective ions in the orthorhombic and monoclinic crystal fields.

The lanthanide chlorides can be used in different areas of science and technology, such as quantum optics, electronics, technological processes for producing the lanthanide metals and their comounds in high purity, etc.

The low-temperature heat capacities of nine lanthanide chlorides, $NdCl_2$, $SmCl_2$, $EuCl_2$, $DyCl_2$, $TmCl_2$, $YbCl_2$, $DyCl_3$, $YbCl_3$ and $LuCl_3$, have been measured in the temperauure range 10–320 K.

Experimental part

Trichlorides were prepared by the reaction between Ln_2O_3 and CCl_4. Dichlorides except $EuCl_2$ were produced by the solid or liquid reaction between $LnCl_3$ and Ln; the reagents were taken in stoichiometric proportions. $EuCl_2$ was obtained by the hydrogen reduction of $EuCl_3$. The characteristics of the substances under investigation are shown in Table 1.

The heat capacity measurements were carried out in an adiabatic microcalorimeter [1] in the temperature range 10–320 K.

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Table 1 Characteristics of prepaeed lanthanide chlorides

Formula	Purity, %	Crystalline modification	Struct. type	Symmetric group	
				space	point
$NdCl_2$	99.56	orthorhombic	$PbCl_2$	Pbnm	D_{2h}
$SmCl_2$	99.62	orthorhombic	$PbCl_2$	Pbnm	D_{2h}
$EuCl_2$	99.50	orthorhombic	$PbCl_2$	Pbnm	D_{2h}
$DyCl_2$	99.63	orthorhombic	SrI_2	Pbca	D_{2h}
$TmCl_2$	99.79	orthorhombic	SrI_2	Pbca	D_{2h}
$YbCl_2$	99.41	orthorhombic	SrI_2	Pbca	D_{2h}
$DyCl_3$	99.86	monoclinic	$AlCl_3$	$C_{2/m}$	C_{2h}
$YbCl_3$	99.75	monoclinic	$AlCl_3$	$C_{2/m}$	C_{2h}
$LuCl_3$	99.82	monoclinic	$AlCl_3$	$C_{2/m}$	C_{2h}

The calorimetric ampoule, made of stainless steel (V = 2.5 cm^3), was put into a copper calorimeter; the temperature was measured with a Pt resistance thermometer. The calorimeter was calibrated against the heat capacity of benzoic acid. The scattering of the experimental points was not worse than 0.2% in the range 50–300 K, 0.5% in the range 20–50 K, and 5% in the range 10–20 K. Systematic uncertainties are about 0.01%.

Results and discussion

The experimental data were treated with the program based on the spline approximation [2]. The program was developed for the treatment of heat capacity data for substances in the condensed phase. To smooth the experimental points with the spline functions, it is necessary to find the weight for every point, so a special procedure based on the least square method was created. The thermodynamic properties were calculated via the spline coefficients.

The standard thermodynamic properties of the investigated substances are summarized in Table 2. The uncertainties include the scattering of the points, the systematic uncertainty of the measurements, the influence of the impurities and also the uncertainty of the C_p extrapolation to $T = 0$.

Analysis of the experimental data

The heat capacities of the chlorides are similar to those of other lanthanide compounds, comprising the lattice heat capacity with an additional contribution caused by the thermal population of the low-lying Stark electronic levels (Schottky anomaly). The Schottky contribution is shown simultaneously with the main lattice

Table 2 Standard thermodynamic data on selected lanthanide chlorides

Formula	C_p^0 (298.15 K)	S^0 (298.15 K)	H^0 (298.15 K) − H^0 (O)
	J·deg^{-1} mol^{-1}		J·mol^{-1}
$NdCl_2$	77.77±0.30	140.1±0.5	17310±60
$SmCl_2$	84.41±0.30	132.2±0.4	18320±60
$EuCl_2$	75.23±0.40	138.3±0.8	16440±90
$YbCl_2$	77.30±0.30	144.2±0.6	17220±60
$TmCl_2$	76.68±0.20	135.1±0.3	17210±40
$AbCl_2$	75.73±0.40	120.0±0.6	16380±80
$DyCl_3$	100.6±0.2	176.6±0.4	22030±40
$YbCl_3$	101.4±0.3	170.3±0.5	21900±60
$LuCl_3$	96.62±0.20	153.0±0.4	20500±40

Table 3 Energies of split Stark levels

	Main term	p_i	E_i, cm^{-1}		Main term	p_i	E_i, cm^{-1}
$SmCl_2$	$^3F_0$	1	0	$TmCl_2$	$^2F_{7/2}$	2	0
	$^7F_1$	1	273			2	60
		1	293			2	113
		1	313			2	171
	$^7F_2$	1	773	$YbCl_3$	$^2F_{7/2}$	2	0
		1	793			2	160
		1	813			2	320
		1	833			2	450
		1	853			2	640

increment in a wide temperature range; these contributions are expected for $NdCl_2$, $SmCl_2$, $DyCl_2$, $TmCl_2$, $DyCl_3$ and $YbCl_3$. The Schottky heat capacity was estimated as the difference between the experimental C_p values for the isostructural paramagnetic and diamagnetic chlorides. $EuCl_2$ and $YbCl_2$ were used as the diamagnetic analogs for the dichlorides ($NdCl_2$ and $SmCl_2$; $DyCl_2$ and $TmCl_2$, respectively) and $LuCl_3$ for the trichlorides.

The energies of the split Stark electronic levels were evaluated for three compounds: $SmCl_2$, $TmCl_2$ and $YbCl_3$ (Table 3)

The point group symmetry is known for the investigated chlorides (Table 1); accordingly, the main-term splitting was calculated. The energy evaluation was based on the general model of the level splitting of the respective ions in the orthorhombic and monoclinic crystal lattice fields. Good agreement was attained for $SmCl_2$, $TmCl_2$ and $YbCl_2$ (Figs 1–3).

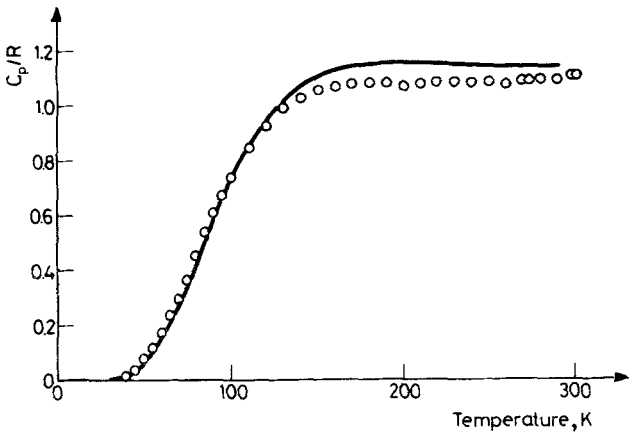

Fig. 1 Schottky anomaly heat capacity of $SmCl_2$, ○ experimental curve; —— theoretical curve

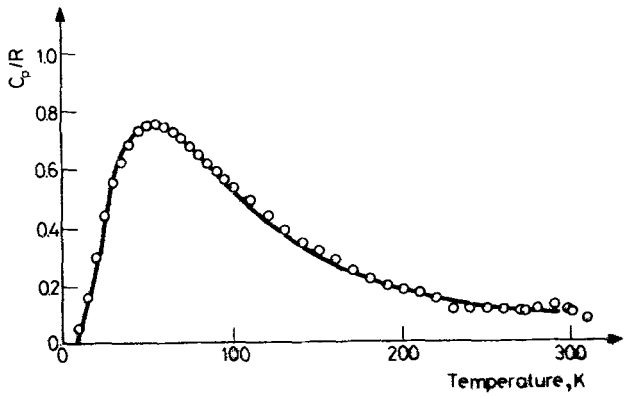

Fig. 2 Schottky anomaly heat capacity for $TmCl_2$. ○ experimental curve; —— theoretical curve

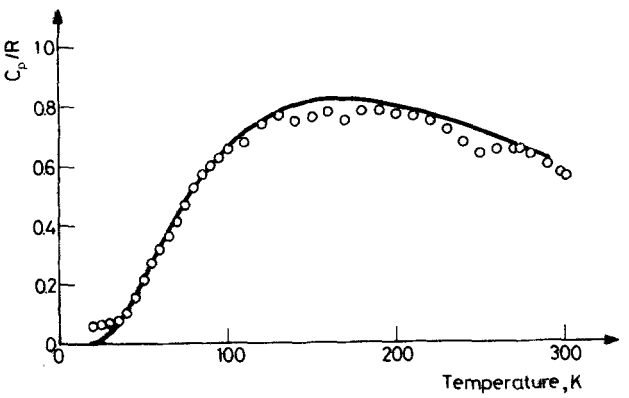

Fig. 3 Schottky anomaly heat capacity for $YbCl_3$. ○ experimental curve; —— theoretical curve

Some differences between the experimental and the theoretical curves were explained by the possible influence of the impurities contained in the $EuCl_2$ and $SmCl_2$ samples.

References

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2 V. S. Iorish and P. I. Tolmach, J. Phys. Chem., 60 (1986) 2538. (in Russian).
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Zusammenfassung — Die Wärmekapazitäten von $NdCl_2$, $SmCl_2$, $EuCl_2$, $DyCl_2$, $TmCl_2$, $DyCl_3$, $YbCl_3$ und $LuCl_3$ wurden im Temperaturbereich 10–320 K mit einem adiabatischen Mikrokalorimeter gemessen. Aus den Ergebnissen wurden die thermodynamischen Standardwerte berechnet. Die Wärmekapazität dieser Chloride setzt sich zusammen aus der Gitter-Wärmekapazität und einem Beitrag, infolge der thermischen Besetzung der niedrig-liegenden Stark-Niveaus (Schottky-Anomalie). Die Schottky-Wärmekapazität wurde als Differenz zwischen experimentellen C_p-Werten isostruktureller para- und diamagnetischer Chloride geschätzt. Die experimentell gefundenen Schottky-Beiträge stimmen gut überein mit den Werten, die für $SmCl_2$, $TmCl_2$ und $YbCl_3$ nach einem verallgemeinerten Modell der Stark-Aufspaltung der Hauptterme der betreffenden Ionen im orthorhombischen bzw. monoklinen Kristallfeld berechnet wurden.

Резюме — С помощью адиабатического калориметра в интервале температур 10–320 К измерены теплоемкости хлоридов двухвалентных неодима, самария, европия, диспрозия, тулия, иттербия и хлоридов трехвалентных диспрозия, иттербия и лютеция. Из полученных данных вычислены стандартные термодинамические свойства. Теплоемкости хлоридов состоят из решеточной теплоемкости и дополнительного вклада, вносимого термической плотностью низколежащих электронных уровней Штарка (аномалия Шоттки). Теплоемкость по Шоттки была определена как различие между экспериментальными значениями C_p для изоструктурных парамагнитных и диамагнитных хлоридов. Экспериментальные величины вкладов по Шоттки для $SmCl_2$, $TmCl_2$ и $YbCl_3$ хорошо согласуются с вычисленными с помощью общей модели основного терма штарковского расщепления соответствующих ионов в кристаллическом поле орторомбической и моноклинной решеток.