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Above room temperature heat capacity and phase transition of lithium tetrahydroborate

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ABSTRACT

New calorimetric determinations of molar heat capacity $C_{p,\mathrm{m}}$ of lithium tetrahydroborate ($LiBH_4$) were performed in order to analyze the origin of the previously observed "anomaly" before the polymorphous transition at 386 K. The above room temperature dependence of $LiBH_4$ $C_{p,\mathrm{m}}$ was measured until approaching the melting point of the compound at 553 K and the abnormal behaviour was attributed to lattice defects independent of the main crystalline phase transition. As a result, lower entropy of the transition $\Delta_{\mathrm{trs}}S = 13.11 \pm 0.23\,\mathrm{J\,K^{-1}\,mol^{-1}}$ than that proposed in literature was obtained, which is in agreement with the observed anisotropy and crystal density decrease before the transition from recent X-ray diffraction indexing. An estimate of the liquid $C_{p,\mathrm{m}}$ of $LiBH_4$ "molten salt" is proposed.

1. Introduction

Interest in lithium tetrahydroborate ($LiBH_4$) is increasing owing to its widespread technological use in laboratories, mainly as a stand matrix for solid-state hydrogen storage and many other applications as a catalyst due to its reducing property. The polymorphic phase transition of the alkali metal (Na, K, Rb and Cs) borohydrides occurs at lower temperature than room one's [1], meanwhile for $LiBH_4$ this transition proceeds above room temperature [2]. Indeed, it was shown by X-ray diffraction and thermal analysis that the compound undergoes a crystalline phase transition from orthorhombic to hexagonal at about $T_{\mathrm{trs}} = 386\,\mathrm{K}$ then it melts around $T_{\mathrm{fus}} = 553\,\mathrm{K}$ [3,4]. The high temperature hexagonal phase has been clarified with more recent X-ray indexing, although it was considered to be tetragonal for over 30 years. Symmetry group suggest a first-order transition during which the tetrahedral $[BH_4]$ anions are reoriented [5].

The thermal stability of the compound has been extensively studied [2–4,6,7] after its discovery in 1940 by Schlesinger and Brown [8] when reacting diborane with ethyl-lithium. To our knowledge, only one published paper, by Gorbunov et al. [3], has reported the above room temperature molar heat capacity $C_{p,\mathrm{m}}$ of the $LiBH_4$ compound up to $T = 450\,\mathrm{K}$. In addition, the above room temperature heat capacity was estimated in JANAF thermochemical tables [9] from the $NaBH_4$ compound and was considered as a single polymorphic solid-phase and in fact has not been reviewed since December 1964. Within the 300–450 K temperature range, Gorbunov et al. [3] found that their differential scanning calorimetry (DSC) measurements were 5% higher than the values obtained from their extended low temperature experiments using adiabatic calorimetry under vacuum. This shift was attributed by the authors to the thermal conductivity of $LiBH_4$ which was not the same (for the two calorimetric runs) due to sample preparation differences: probably the morphology of the powders was different. These authors distinguish two different behaviours of $C_{p,\mathrm{m}}$ within the 225–395 K temperature range: (i) an "abnormal" increase from $T = 225\,\mathrm{K}$ up to $T = 381\,\mathrm{K}$ and (ii) an isothermal event corresponding to the phase transition of $LiBH_4$ that occurred at $386.4 \pm 1\,\mathrm{K}$. Thus, there is only one determination of $C_{p,\mathrm{m}}$ for the hexagonal crystalline phase (high temperature polymorphic form) characterized by a short temperature range (about 170 K) and limited at a maximum of 450 K [3]. Even though some studies were related to the liquid phase, none of them determined the heat capacity of the $LiBH_4$ liquid (above 553 K). Additional experimental calorimetric data to evaluate the reliability and supplement the previous determinations are highly desirable in terms of thermodynamic description of this compound. Moreover, by analyzing the above room temperature heat capacity reported by Gorbunov et al. [3], the cause for the increase in the $C_{p,\mathrm{m}}$ observed at about 360 K before the polymorphous transition needs to be understood. In order to clarify this point, we carried out our own $C_{p,\mathrm{m}}$ measurements above room temperature with the following aims: (i) check the reality of this

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increase in $C_{p,\mathrm{m}}$ before the transition, (ii) determine a new value for the enthalpy of the transition, (iii) define a complete $C_{p,\mathrm{m}}$ function for the hexagonal phase up to its melting point. Finally, from the hexagonal phase heat capacity, the $C_{p,\mathrm{m}}$ of the liquid phase can be estimated based on the behaviour of similar high temperature molten salts of known heat capacity.

2. Experimental

Single-phase $LiBH_4$ was purchased from Alfa Aesar (mass fraction 0.981 assay) and stored in its delivery flask in a glove box equipped with permanent argon flow regeneration (H_2O/O_2, volume fraction < 10^{-5}). The original impurities were not identified and it was shown by X-ray diffraction that these impurities do not form any solid solutions with the main substance. Heat flow measurements were performed using a differential scanning calorimeter (D.S.C, TA Instrument 2920) under argon flow (50 cm^3 min^{-1}, 0.999999 purity). The standard pressure was $p^\circ = 1$ bar. Aluminium containers with a lid in the form of hermetic crimped pans were used. Quantitative calorimetric calibration of the heat capacity was carried out using monocrystalline alumina (sapphire) previously dried at 1173 K just before use. Temperature and enthalpy calibrations were carried out using tin and indium (0.9999 purity) standards by considering their melting temperature and enthalpy as compiled in literature [10]. The uncertainty of heat capacity measurements are thus within 2.5% at room temperature, a value that reduces to 0.2% when the temperature rises.

The pans were weighed and loaded with the samples in the glove box in order to minimize the atmospheric exposure time. The pan/samples were loaded in a closed vessel in the glove box, then transported and loaded immediately in the DSC under argon reflux. Empty pans were also handled in the same way as for the samples to avoid any undesirable effect. Before the scanning cycles, $LiBH_4$ samples were desorbed in the calorimeter for 4 h under primary vacuum at 523 K. Pumping flow contaminations were reduced using a liquid nitrogen trap. For the molar heat capacity, $C_{p,\mathrm{m}}$, determinations, at least 3 scanning cycles were used for all samples and the measurements were found to be reproducible beyond 3 cycles. Hence, only the third and last recording was used for the determination of $C_{p,\mathrm{m}}$. The reference (sapphire) was found to deviate practically by a constant factor with some asymptotic behaviour at the end of the recording. But this should not influence the results as the correction was made instantaneously, step-by-step, when knowing the $C_{p,\mathrm{m}}$ of the reference.

The $C_{p,\mathrm{m}}$ determinations were performed using two different and separate scanning methods: "linear temperature ramp" (Fig. 1) and "enthalpy method" (Fig. 2). Recordings of the reference (sapphire) and of the empty pan (baseline) were made before and after each experiment to guarantee reproducibility of the measurements. The weight of the samples – determined in the glove box – was checked after each measurement and found to be constant within the balance precision limit.

In the first case, transient isothermal periods at the start and end of each scan, are imposed to reach a steady-state dynamic equilibrium of the system. A scan rate of 5 K min^{-1} was chosen. The molar heat capacity of the sample $C^{\mathrm{s}}_{p,\mathrm{m}}$ was determined using the following formula knowing the mole numbers of the sample (n_s) and of the reference (n_ref):

$$C^{\mathrm{s}}_{p,\mathrm{m}} = C^{\mathrm{ref}}_{p,\mathrm{m}} \cdot \frac{\Delta Y_\mathrm{o} + \Delta Y_\mathrm{s}}{\Delta Y_\mathrm{o} + \Delta Y_\mathrm{ref}} \frac{n_\mathrm{ref}}{n_\mathrm{s}} \tag{1}$$

Relation in which ΔY_s, ΔY_ref, ΔY_o, are the instantaneous heat flows for the sample, the reference and the empty pan, respectively, with the convention used in the reference [11]. $C^{\mathrm{ref}}_{\mathrm{p,m}}$ is the molar heat capacity of the reference taken from the thermochemical tables [12].

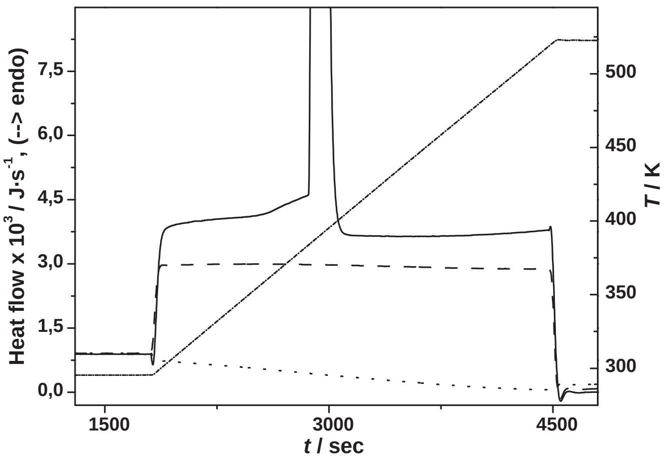

Fig. 1. DSC heat flow measurements versus time t using the temperature T linear ramp method: —, $LiBH_4$ sample; – –, sapphire reference; · ·, baseline.

In the enthalpy method, the temperature is programmed as short ramps of 20 K with a scan rate of 5 K min^{-1}. The peak transition is arranged to be inside this temperature interval. Between each ramp an isothermal hold of 120 s is imposed. By integrating the heat flow areas, the values are corrected to the baseline and reported to the reference for heat capacity data as measured for a mean temperature. This method is used mainly to check the previous continuous dynamic method since it allows the average molar heat capacity of the sample, $\overline{C^{\mathrm{s}}_{p,\mathrm{m}}}$, to be calculated in a temperature interval $\Delta T = 20$ K, using the formula:

$$\overline{C^{\mathrm{s}}_{p,\mathrm{m}}} = \overline{C^{\mathrm{ref}}_{p,\mathrm{m}}} \cdot \frac{\Delta Q_\mathrm{o} + \Delta Q_\mathrm{s}}{\Delta Q_\mathrm{o} + \Delta Q_\mathrm{ref}} \frac{n_\mathrm{ref}}{n_\mathrm{s}} \tag{2}$$

where ΔQ_s, ΔQ_ref, ΔQ_o, are the amounts of heat required to increase the temperature by a 20 K step for the sample, reference and empty pan, respectively, as described elsewhere [11].

3. Results and discussion

3.1. *$LiBH_4$ solid phases*

The above room temperature heat capacities of the $LiBH_4$ compound obtained using the two methods are presented in Fig. 3. Twelve experimental $C_{p,\mathrm{m}}$ values were determined using the enthalpy method. The experimental $C_{p,\mathrm{m}}$ values obtained using

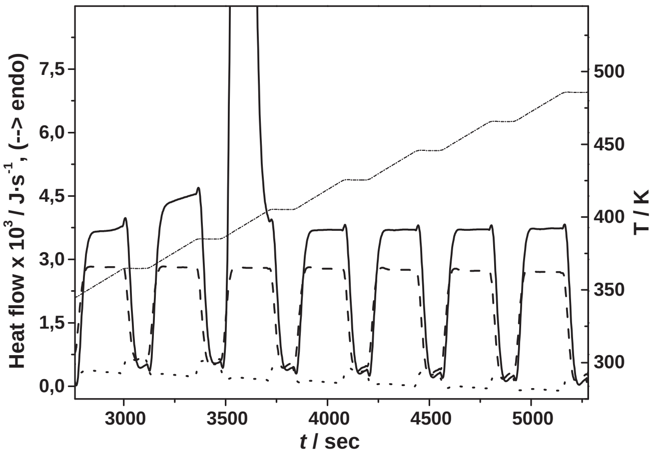

Fig. 2. DSC heat flow measurements versus time t using the enthalpy method: —, $LiBH_4$ sample; – –, sapphire reference; · ·, baseline.

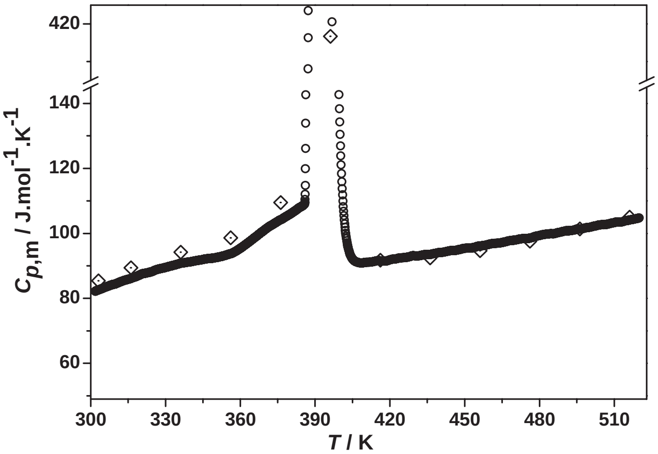

Fig. 3. High-T experimental molar heat capacity of $LiBH_4$ compound: ○, linear ramp and ◇, enthalpy methods.

the linear ramp method are in close agreement with the values obtained by the enthalpy method within 1% standard deviation. As there is very good agreement between the two methods, only the results obtained by the linear ramp method are retained for the following analysis. The apparent $C_{p,\mathrm{m}}$ increase has a value of 853.6 J K^{-1} mol^{-1} at the apex with a hysteresis of about 12 K, a value which is higher than the previously reported thermal analysis and heat capacity data using lower heating rates [2,3].

Fig. 4 presents a comparison between our results and those previously obtained in the literature. It shows good agreement between our determinations of $C_{p,\mathrm{m}}$ and the results obtained by Hallett and Johnston [6] and Gorbunov et al. [3], slightly extended from low temperature data. Above room temperature, the $C_{p,\mathrm{m}}$ curve seems to present an inflexion point around 354 K then undergoes an increase which is independent of the main transition (Fig. 3). In agreement with Gorbunov et al. [3] results, the presence of an "abnormal" part in the $C_{p,\mathrm{m}}$ curve is also observed in our own measurements (Fig. 4) but it is less pronounced and, consequently, presents a smaller heat capacity decrease step at the phase transition (about 8 J K^{-1} mol^{-1}) between the two polymorphic crystals. The greater increase in the abnormal part in the previous study, compared to our observations, is probably due to greater residual desorption – water or some kind of hydroxide –, overlapping with the phase transition thermal effect. Probably the Gorbunov et al. [3] sample lost some mass in vacuum. Unfortunately, the authors did not discuss this phenomenon nor the possibility of performing cyclic measurements. Therefore, this feature could not be totally attributed to the impurities in the compound since the samples in our case were desorbed at 523 K under vacuum before the measurements. As this increase was observed to be reproducible after several cycles, the present "abnormal" behaviour should be attributed to another phenomenon, unless some new re-adsorption occurred cyclically after introducing the sample in the calorimeter. The fact cannot be ignored that in case of high purity prepared samples, the vacuum or flow gas quality in the calorimeter may be insufficient to prevent some re-adsorption reactions after the desorbed stage when cycling, with a cycle duration being about 4 h. The heat flow signal became distorted beyond 6 cycles.

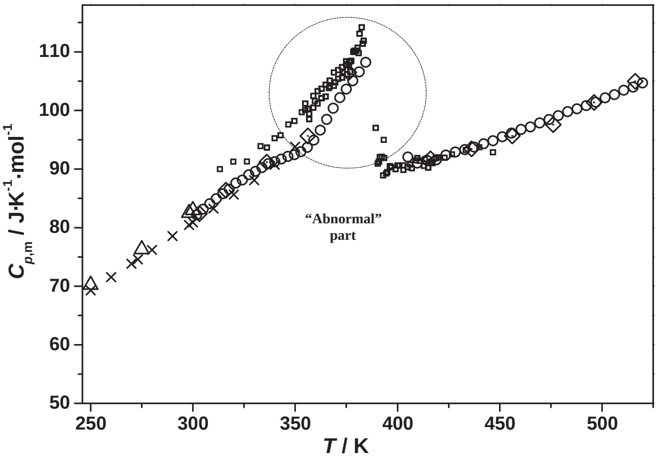

Fig. 4. Experimental heat capacity data of $LiBH_4$ compound. Low-T: △, Nernst calorimetry [6]; ×, Adiabatic calorimetry [3]. High-T: □, DSC [3]; ○, linear ramp and ◇, enthalpy methods [this work].

From recent crystallographic data, a complex structural evolution as a function of temperature was reported by Filinchuk et al. [13]. Order–disorder transition was suggested owing to the lowering of the symmetry in the crystal cell where a disorder model was supported for the hexa-phase. Thermal expansion was reported by the authors to be nonlinear for the ortho-phase with a higher anisotropy near the transition. According to Raman data, the observed increase in $C_{p,\mathrm{m}}$ before the main transition could be attributed to an increase of the number of vibrational levels for [BH_4] group in the same crystal lattice, followed by a sudden structural transformation at the transition. Indeed a broadening of Raman lines, notably for stretching mode, was observed before the transition (from 360 K to 380 K) in the line width diagram of Gomes et al. [14] along with the disappearance of the two observed peaks at lower temperature. This is a priori in agreement with the negative slope at the transition line obtained from Pistorius' high pressure phase diagram [15] but in contradiction with his X-ray indexing. Another cause of heat capacity increase could be the increase in defects due to the existence of a non-stoichiometric composition domain. Regardless of the causes for this phenomenon, the abnormal increase in the $C_{p,\mathrm{m}}$ could not be considered to be part of the main transition as proposed by Gorbunov et al. [3]. This anomaly could influence drastically the way the transition temperature and enthalpy are determined. Indeed, the onset position and the area under peak which could be integrated will be strongly affected by this anomaly. Above the transition temperature, the heat capacity of the hexagonal crystal once again follows a regular trend.

Table 1 presents some experimental data and corresponding fitted values of $C_{p,\mathrm{m}}$ with an average fractional deviation, $10^2 \cdot |C_{p,\mathrm{expt}} - C_{p,\mathrm{fit}}|/C_{p,\mathrm{fit}}$, of about 0.12. Standard deviations as well as relative error of the experimental values are presented in Fig. 5. Hence, the proposed heat capacity of $LiBH_4$ is a non-linear least squares fit using a second order polynomial with a T^{-2} term from room temperature until the approach of the compound melting point. According to Eq. (3), the $C_{p,\mathrm{m}}$ analytical expression is defined in three T ranges: above room T orthorhombic-phase, "abnormal" orthorhombic-phase and short T range hexagonal-phase. The results obtained are summarized in Table 2. The calculated average value of $C_{p,\mathrm{m}}$ at 298 K from low temperature data is found to agree with the interpolated value in our measurements within 0.2%.

$$C_{p,\mathrm{m}}(T) = \mathrm{a} + \mathrm{b}T + \mathrm{c}T^2 + \mathrm{d}T^{-2} \tag{3}$$

The integrated enthalpy for the polymorphous transition is $\Delta_{\mathrm{trs}}H = 5069 \pm 76$ J mol^{-1} at the measured temperature of the transition 386.6 ± 0.1 K. As the thermocouples and their electrical chain in this temperature range cannot be calibrated with an accuracy of less than 1 K, an uncertainty equal to ±1 K ($T_{\mathrm{trs}} = 386.6 \pm 1$ K) has been proposed. The present enthalpy increment could not be directly compared to the value obtained by Gorbunov et al. [3] from the monitored heat capacity as the interpretation of the phase transition region is different. However, a good agreement is to be emphasized when considering only the Gorbunov et al.

Table 1
Experimental and fitted molar heat capacities, $C_{p,\mathrm{m}}$/J K^{-1} mol^{-1}.

T/K	Experimental	Fitted
298	81.51[a]	81.63
310	84.51	84.94
320	87.33	87.24
330	89.53	89.59
340	91.21	91.28
350	92.47	92.72
360	95.46	95.34
370	101.20	100.77
380	106.02	105.99
386.6	Transition, $\Delta_{\mathrm{trs}}H = 5.069 \pm 0.076$ kJ mol^{-1}	
410	91.06	91.19
420	91.83	91.99
430	93.09	92.97
440	94.12	94.08
450	95.43	95.29
460	96.70	96.57
470	97.95	97.90
480	99.14	99.26
490	100.69	100.63
500	101.90	101.97
510	103.30	103.30
520	104.78	104.57
530		105.79
540		106.94
550		108.01
553	Fusion[b], $\Delta_{\mathrm{fus}}H = 8.18 \pm 0.3$ kJ mol^{-1}	

[a] Average value from low-T heat capacity data [3,6].
[b] Assessed literature value [16,17].

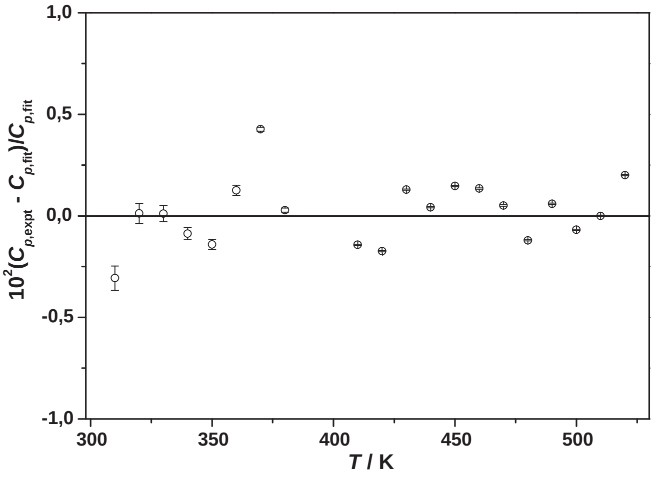

Fig. 5. Relative deviations of some experimental heat capacity $C_{p,\mathrm{expt}}$ values from fitted values $C_{p,\mathrm{fit}}$ as a function of temperature.

main transition peak (5055 ± 15 J mol^{-1}). The calculated entropy of the transition is $\Delta_{\mathrm{trs}}S = 13.11 \pm 0.23$ J K^{-1} mol^{-1}. This value is lower than that determined by Pistorius [15], *i.e.* 16.5 J K^{-1} mol^{-1}.

If one considers the abnormal (*abn*) increase as a part of the transition process (see Fig. 4), then a value of $\Delta_{\mathrm{trs+abn}}H = 5416 \pm 91$ J mol^{-1} is found starting from $T = 354$ K. In that case, the ortho-phase can be described by only one equation. Indeed, the fitted equation for the $C_{p,\mathrm{m}}$ in the temperature range (298–354 K) in Table 2 could be extended until $T = 386$ K. Note that the value of $\Delta_{\mathrm{trs+abn}}H$ is still lower than the total value as reported by Gorbunov et al. [3] (6229 ± 84 J mol^{-1}) which could be due to the fact that their integration starts from $T = 225$ K (instead of $T = 354$ K in our case). Taking into account difficulties mentioned by the authors for the integration of this first part, the comparison could be tricky.

3.2. LiBH$_4$ liquid phase

The LiBH$_4$ compound is a salt-like compound due to the hydride character of the [BH$_4^-$] anionic component. Available models for estimating the heat capacity of liquid phases, taking into account the anionic and cationic contributions, are not viable for our system due to lack of data. In spite of the "apparent" instability of the hydrides after melting due to hydrogen gas release [2], the $C_{p,\mathrm{m}}$ of the liquid is considered to be stable under standard equilibrium conditions (at p° of H$_2$ in equilibrium with H dissolved in the liquid) as observed in related experiments under H$_2$ with pressure increasing from 1.0133 to 10.133 bar [4]. By analogy, $C_{p,\mathrm{m}}$ of the liquid was estimated by considering the increase in the value from the solid to the liquid that observed in the two high-T molten salts LiF and LiBF$_4$, the $C_{p,\mathrm{m}}$ of which was determined experimentally [18,19]. This assumption is based on the comparison of the physical and chemical properties (structure close to LiBF$_4$ and ionic radius of the anion BH$_4^-$ close to F$^-$). A mean value is adopted from the barycentric formula for the different compounds:

$$C_{p,\mathrm{m}}(\mathrm{LiBH_4, l}) = C_{p,\mathrm{m}}(\mathrm{LiBH_4, s}) \times \Gamma \tag{4}$$

where Γ is an average factor assuming an increase in $C_{p,\mathrm{m}}$ from solid to liquid of the two salts LiBF$_4$ and LiF independently of their melting temperatures [20]. This factor could be described according to the formula:

$$\Gamma = \frac{\{C_{p,\mathrm{m}}(\mathrm{LiBF_4, l})/C_{p,\mathrm{m}}(\mathrm{LiBF_4, s})\} + \{C_{p,\mathrm{m}}(\mathrm{LiF, l})/C_{p,\mathrm{m}}(\mathrm{LiF, s})\}}{2} \tag{5}$$

From the reference values of $C_{p,\mathrm{m}}$(liquid) and $C_{p,\mathrm{m}}$(solid) used in this calculation (Table 3), given at melting temperature of corresponding compounds, Eq. (5) leads to $\Gamma = 1.1515$. Following the above assumption and knowing the $C_{p,\mathrm{m}}$ of the hexagonal phase for temperatures close to its melting point (108.3 J K^{-1} mol^{-1}), a value

Table 2
Fitted molar heat capacities of the LiBH$_4$ phases as a function of temperature, $C_{p,\mathrm{m}}$/J K^{-1} mol^{-1}, according to Eq. (3).

Phase	T/K range	a	b	$c \times 10^3$	$d \times 10^{-6}$
Ortho-phase	298–354	23.479	0.5439	−0.7885	−3.010
	354–386	−29738.586	107.620	−108.78	672.460
Hexa-phase	386–553	−494.068	1.594	−1.13	20.500

Table 3
Molar heat capacity $C_{p,\mathrm{m}}$/J K^{-1} mol^{-1} values of the solid and liquid salts LiBF$_4$ and LiF used as reference in the calculations and the estimated value for liquid LiBH$_4$.

At the phase boundary	T_{fus}/K	Solid phase	Liquid phase	Ref.
LiF	1122	63.2	64.9	[18]
LiBF$_4$	583	131.5	167.8	[19]
LiBH$_4$	553	108.3	124.7	[This work]

of 124.7 J K^{-1} mol^{-1} is found for the molar heat capacity of $LiBH_4$ molten salt which is assumed to be constant versus temperature.

4. Conclusion

The above room heat capacity of the $LiBH_4$ compound, containing less than 0.02 mass fraction impurities, has been measured. This work proposes a new set of values for selected heat capacities for the different condensed phases (orthorhombic, hexagonal and liquid). Improvement is clear for the hexagonal phase in the short temperature range of its existence from 386.6 K until melting at 553 K. The observed anomaly before the polymorphic phase transition at 386.6 K has been discussed and attributed to an "abnormal" trend independent of the main transition. This trend is probably a result of the increase of crystal defects (non-cubic lattice) for the ortho-$LiBH_4$ compound related to larger librational motions of the tetrahedral $[BH_4]$ (less hindering Li effect compared to other alkali metals). More focus on this complex region is needed in order to clarify on the nature of the increase of the molar heat capacity which could contribute to the understanding of the origin of the disorder phenomena in crystalline phases. Based on our results, the previously considered enthalpy increment determined by the integration method, as well as the transition temperature needs to be modified. Consequently, a new enthalpy for the polymorphous transition is proposed (5069 ± 76 J mol^{-1}) with a transition temperature of 386.6 ± 1 K. On the basis of the results obtained, the Gibbs free energy function of $LiBH_4$ condensed phases can be assessed, providing relevant insights into the modelling of reactions involving the desorption and chemisorption of hydrogen.

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