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HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF THE NON-LINEAR OPTICAL MATERIAL α-$LiIO_3$ CRYSTAL *

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ABSTRACT

The heat capacity of α-$LiIO_3$ crystal, a kind of new non-linear optical material, has been measured with a fully automated adiabatic calorimeter in the temperature range from 13 to 320 K. The calorimetry system is briefly described. There is no indication of any phase transition or thermal anomaly in this temperature region for the present crystal. The experimental heat capacity data have been fitted to a smoothed curve with the aid of the effective frequency distribution method, and heat capacities below 13 K have been derived by extrapolating the fitting curve down to 0 K. The standard molar thermodynamic functions of the present compound between 0 and 320 K have been calculated from the C_p data and tabulated at selected temperatures. The values of $C_p^\circ(T)$, $S^\circ(T)-S^\circ(0)$, $[H^\circ(T)-H^\circ(0)]/T$, and $-[G^\circ(T)-H^\circ(0)/T$ at $T=298.15$ K are 99.56_8, 109.75_3, 58.05_6, and 51.69_7 J K^{-1} mol^{-1}, respectively.

INTRODUCTION

The lithium iodate ($LiIO_3$) crystal exists in two stable crystalline forms at ambient temperature and under normal atmosphere. One is β-$LiIO_3$, the space group of which is $C_{4h}^4(P4_2/n)$ [1], and the parameters of its unit cell are $a = 9.733$ Å and $c = 6.157$ Å. The β-$LiIO_3$ has a center of symmetry. The other form is the electropolar crystal α-$LiIO_3$; the space group is $C_6^6(P6_3)$ [2] and the crystal data are $a = 5.482$ Å, $c = 5.171$ Å.

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The α-$LiIO_3$ (abbreviated to α-LI) crystal has been widely used as a kind of new non-linear optical material [3,4] due to its good non-linear optical characteristics. In China it has been successfully utilized recently for ultrasonic inspection and thickness-measuring techniques [5]. Under the influence of an electrostatic field, α-LI manifests various unique behaviors which deserve extra attention [6]. A large number of studies on the electrical and optical properties of α-LI have already been reported [7,8]. However, the thermodynamic properties of α-LI have not been studied. Therefore, as a part of the research project for this material, we measured precisely the low-temperature heat capacities of α-LI by means of an automated adiabatic calorimeter and determined the standard thermodynamic functions of α-LI in the temperature range from 0 to 320 K on the basis of the heat capacity measurements.

EXPERIMENTAL

Sample preparation and characterization

The α-LI crystal sample used in this investigation was grown from a solution prepared by the reaction of Li_2CO_3 with HIO_3

$$Li_2CO_3 + 2\ HIO_3 = 2\ LiIO_3 + H_2O + CO_2$$

The α-LI was recrystallized by slow evaporation of the aqueous solution of $LiIO_3$ at 345–355 K and pH 2.5–3.5. The polycrystalline α-LI crystal thus obtained was then cleaned with distilled water and absolute alcohol followed by drying at ambient temperature under vacuum for 2 h until the water and alcohol left on the surfaces of the crystal particles were completely removed. The final product looked like white prisms with a size of ~ 3 mm. Chemical analysis showed that the purity of the α-LI crystal thus obtained was 99.99 wt.% and X-ray diffraction demonstrated that the sample was in the α-phase.

Calorimeter

Heat capacity measurements were performed with an automated adiabatic calorimeter [9]. As shown in Fig. 1, the present calorimeter apparatus consisted mainly of three vacuum spaces designated as the outer, middle, and inner vacuum cans, respectively. The three spaces can be independently evacuated to 10^{-4} Pa or lower. As the outer vacuum can was immersed in liquid nitrogen, its temperature always remained at about 77 K. The middle can with a nitrogen tank, was used to cool the inner can to solid nitrogen temperature. The inner can was equipped with a helium tank and a spiral copper tube through which cold helium gas evaporated from the tank

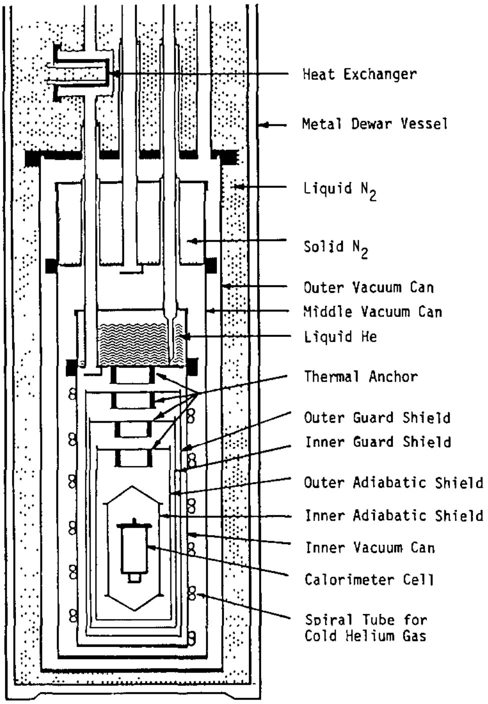

Fig. 1. Sectional view of the adiabatic calorimeter for heat capacity measurements between 13 and 520 K.

circulated and then exited through the cryostat. In the inner can there were housed two guard shields, two adiabatic shields, and the innermost calorimeter cell. The adiabatic condition between the cell and its surroundings was realized by the combined functions of the four shields, on the peripheries of which constantan heating wires were wound and chromel–constantan differential thermocouples mounted. The inner adiabatic shield was divided into three parts, viz. the bottom, side, and top part, respectively, while the outer adiabatic shield consisted of two sections: the side and the lid with a thermal anchor. The adiabatic temperature control for the four shields was automated by using d.c. amplifiers and proportional mode temperature controllers. Under adiabatic conditions, the temperature of the calorimeter cell could be kept constant within 1 mK for several hours during the experimental period.

The calorimeter cell consisted of a sample container, a platinum resistance thermometer, a heater for energy supply, and a thermocouple sleeve. The cell was suspended in a high vacuum from the top of the inner shield by a teflon-coated constantan wire. The cell [10] used for the present study was made of gold-plated copper and had an internal volume of 30 cm^3; four gold-plated copper partition walls of 0.2 mm thickness were soldered inside the cell to aid in the heat distribution from the cell heater and the subsequent reestablishment of thermal equilibrium. The flange with an indium O-ring gasket was used for the vacuum-tight closure between the lid and the main body of the cell. The calorimeter heater and the platinum resistance thermometer were mounted together in the re-entrant well of the calorimeter cell with Wood's alloy.

The temperature of the calorimeter cell was measured by the platinum thermometer, the temperature scale of which is based on the IPTS-68. The resistance of the thermometer was measured by an a.c. resistance bridge.

A constant d.c. current generator was used for the energy supply. A digital multimeter and a universal counter were used for the electric energy and the time interval measurements, respectively.

A personal computer was used for the automatic data-acquisition system. All the equipment was operated and controlled by the computer, hence the heat capacity measurements were performed automatically, including heat-on and heat-off for the calorimeter cell, monitor of the adiabatic conditions, and judgment of the equilibrium state.

Heat capacity measurement

The heat capacities of α-LI crystal were measured in the range 13–320 K with the adiabatic calorimeter described above. The amount of sample loaded in the calorimeter cell amounted to 46.0910 g after a buoyancy correction assuming a sample density of 3.3 g cm^{-3}. This mass is equal to 0.253465 mol based on its molar mass of 181.8437 g mol^{-1}. To facilitate rapid thermal equilibration, a small amount of helium gas was introduced into the calorimeter cell through a capillary tube after evacuation of the air. The entrance of the tube was then sealed with solder.

Heat capacity measurements of the sample were performed as a function of temperature by the standard discrete heating method. In this intermittent mode the procedures of heat capacity measurement involve determination of the amount of energy supplied to the calorimeter cell and the temperature increment caused by the energy input, hence the sequence of measurements was composed of two successively alternating periods. One was the drift period during which the temperature of the calorimeter cell was observed as a function of time, and the other was the energy input period during which a definite amount of electrical energy was supplied to the calorimeter cell. The supplied energy was determined on the basis of measurements of the voltage and current across and through the calorimeter heater as well as the interval of the energy input.

Once the sample cell was mounted in the calorimeter, the cryostat was evacuated and the adiabatic control was suitably adjusted. The personal computer repeated the measurement cycles for temperature and energy input in the above sequence and printed out the molar heat capacity at the end of each cycle by using the stored empty-cell data and keyed-in mole factor of the sample, with a small correction for the heat capacity of the conduction helium gas sealed in the calorimeter cell.

The operational criterion for thermodynamic equilibrium in our measurements was that the temperature of the calorimeter cell was stationary to within about ±0.1 mK in 10 min. The normal length of time needed to reach such a drift or the thermal relaxation time depended on the temperature region. After each energy input thermal equilibrium in the calorimeter cell was attained in about 5 min below 15 K, 10 min at about 20 K, 15 min at about 30 K, 20 min at about 50 K, and 25 min above 100 K.

RESULTS AND DISCUSSION

Heat capacities of the α-LiIO$_3$ crystal

The measured molar heat capacities of the α-LI crystal are shown in Fig. 2 and listed in chronological sequence in Table 1, in which four series of measurements and 136 experimental points are all included. The contribution of the sample to the total heat capacity, including that of the empty cell, was 56% at 14 K, 44% at 20 K, 42% at 100 K, 49% at 200 K, and 52% at 300 K; the average was about 50% over the entire temperature range. The precision of the heat capacity measurements was estimated to be about ±0.1% in the experimental temperature region. The temperature increment due to each energy input, as may be inferred from adjacent mean temperatures in Table 1, was 1–3 K, which is small enough to permit the curvature correction of heat capacity to be ignored in comparison with the experimental error.

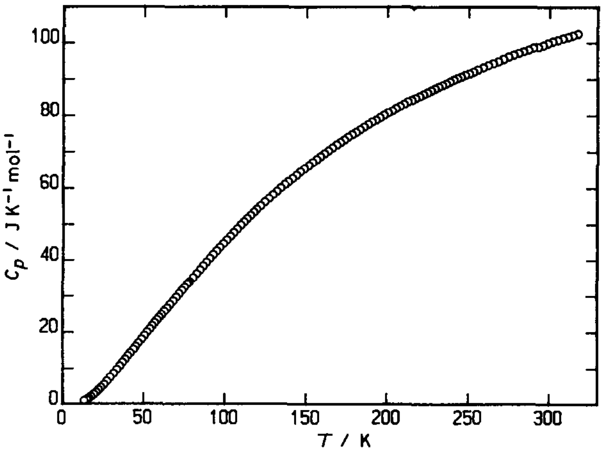

Fig. 2. Molar heat capacity of the α-LiIO$_3$ crystal in the range from 13 to 320 K.

TABLE 1

Experimental molar heat capacities of α-$LiIO_3$ crystal

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
Series 1					
78.585	33.94	151.672	66.28	229.608	87.38
80.723	35.08	154.058	67.05	231.944	87.88
82.891	36.21	156.421	67.85	234.271	88.35
84.999	37.31	158.851	68.70	236.589	88.78
87.053	38.41	161.347	69.49	238.899	89.28
89.059	39.45	163.822	70.28	241.200	89.77
91.103	40.50	166.277	71.09	243.492	90.22
93.184	41.56	168.805	71.88	245.776	90.60
95.221	42.56	171.223	72.55	248.209	91.13
97.303	43.60	173.623	73.32	250.792	91.46
99.432	44.61	176.010	74.04	253.361	91.99
101.521	45.64	178.379	74.72	256.244	92.57
103.651	46.67	180.870	75.36	259.434	93.13
105.822	47.72	183.370	76.10	262.611	93.73
107.956	48.75	185.853	76.83	265.775	94.25
110.056	49.72	188.545	77.57	268.926	94.80
112.124	50.66	190.764	78.18	272.062	95.42
114.162	51.51	193.287	78.75	275.173	96.09
116.172	52.38	195.794	79.41	278.259	96.61
118.156	53.25	198.287	80.11	281.333	97.14
120.115	54.09	200.769	80.76	284.396	97.59
122.369	55.06	203.236	81.31	287.446	97.99
124.912	56.15	205.689	81.93	290.482	98.59
127.418	57.18	208.130	82.55	293.504	98.82
129.891	58.18	210.560	83.11	296.518	99.28
132.331	59.16	212.978	83.76	299.526	99.81
134.743	60.10	215.387	84.26	302.584	100.35
137.126	61.05	217.782	84.79	305.697	100.70
139.483	61.95	220.167	85.30	308.798	101.16
141.902	62.82	222.541	85.86	311.890	101.54
144.382	63.72	224.906	86.35	314.972	102.00
146.836	64.61	227.262	86.83	318.048	102.39
149.266	65.44				
Series 2					
61.579	24.83	68.677	28.66	74.089	31.59
63.297	25.76	70.538	29.67	75.791	32.49
64.954	26.64	72.340	30.64	77.449	33.39
66.749	27.62				
Series 3					
44.222	15.23	51.050	19.01	57.382	22.56
45.663	16.05	52.746	19.99	58.808	23.33
47.349	16.95	54.359	20.88	60.186	24.10
49.258	17.99	55.901	21.74		

TABLE 1 (continued)

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
Series 4					
14.023	0.88	22.909	3.91	34.033	9.61
15.481	1.25	24.404	4.60	35.854	10.61
16.743	1.61	26.109	5.42	37.586	11.59
18.180	2.06	28.004	6.37	39.248	12.52
19.808	2.65	30.013	7.42	40.858	13.48
21.385	3.26	32.093	8.54	42.393	14.24

From Fig. 2, it is obvious that the plot of experimental molar heat capacity as a function of temperature gives a completely smooth curve with no sign of any phase transition or thermal anomaly.

Curve-fitting of the C_p data

Since the present compound does not exhibit any heat capacity anomalies in the crystalline state, the observed C_p data should principally be described on the basis of lattice dynamics. In order to fit the C_p data to a smoothed curve, we adopted "the effective frequency-distribution method" [11]. Prior to its application to the present compound we shall briefly describe the principle of this method.

The observed heat capacities have been determined not at constant volume but at constant pressure. Thus C_p can be represented by the equation

$$C_p = C_{v,trans} + C_{v,rot} + C_{v,intra} + (C_p - C_v) \qquad (1)$$

where $C_{v,trans}$ and $C_{v,rot}$ indicate contributions from the translational motion and the overall rotation of a molecule, and $C_{v,intra}$ is the contribution from the intramolecular vibrations, while the $(C_p - C_v)$ term corresponds to the correction for the expansion work.

Since the present molecule consists of five atoms, the total degrees of freedom is fifteen. Among them, three degrees of freedom for the monatomic Li^+ cation and three degrees of freedom for the pyramidal IO_3^- anion can be attributed to $C_{v,trans}$, while an additional three degrees of freedom contribute to $C_{v,rot}$. The remaining six degrees of freedom are associated with $C_{v,intra}$ for the anion. The normal mode frequencies of the six degrees of freedom can principally be detected by spectroscopic methods such as IR and Raman spectroscopies because they belong to the optical mode. As the translational freedom belongs to the acoustic mode, its normal mode frequencies have a wide distribution from zero to several hundred cm^{-1} in terms of wavenumber. Although the rotational freedom belongs to the optical mode, its normal mode frequencies are known to have a wide distribution. On the other hand, the correction term $(C_\mathrm{p} - C_\mathrm{v})$ is given by the thermodynamic formula

$$C_\mathrm{p} - C_\mathrm{v} = \frac{\alpha^2 VT}{\beta} \tag{2}$$

where α is the thermal expansion coefficient, V the molar volume, and β the isothermal compressibility. In the absence of the related physical quantities, the quasi-thermodynamic relation

$$C_\mathrm{p} - C_\mathrm{v} = AC_\mathrm{p}^2 T \tag{3}$$

is used where A is a constant. Instead of direct calculation of eqn. (3), the effective frequency distribution method [11] includes effectively the $(C_\mathrm{p} - C_\mathrm{v})$ contribution in the frequency spectrum. Therefore, the total degrees of freedom sometimes becomes slightly larger than the exact degrees of freedom for a given molecule.

The six degrees of freedom arising from the internal vibrations have been detected by IR and/or Raman spectroscopy [12]: the $\tilde{\nu}_1(A_1)$ mode $= 754$, $\tilde{\nu}_2(A_1) = 373$, $\tilde{\nu}_3(E) = 774$ and $\tilde{\nu}_4(E) = 332/355$ cm^{-1}. The contributions from these normal mode frequencies to the heat capacity at temperature T_i can be calculated from

$$C_{\mathrm{v,intra}}(T_i) = R \sum_{j=1}^{6} E(\tilde{\nu}_j, T_i) \tag{4}$$

where R is the gas constant and $E(\tilde{\nu}_j, T_i)$ indicates the Einstein heat-capacity function

$$E(\tilde{\nu}_j, T_i) = \left(\frac{h\tilde{\nu}_j}{kT_i}\right)^2 \frac{\exp(h\tilde{\nu}_j/kT_i)}{\left[\exp(h\tilde{\nu}_j/kT_i) - 1\right]^2} \tag{5}$$

where $\tilde{\nu}_j$ is the jth normal mode frequency, h the Planck constant, and k the Boltzmann constant. The heat capacity given by eqn. (4) was subtracted from the observed C_p value at T_i. The difference thus obtained is simply designated hereafter as the lattice heat capacity, $C_{\mathrm{lat}}(T_i)$. This quantity consists of the contribution from six translational and three rotational degrees of freedom and the $(C_\mathrm{p} - C_\mathrm{w})$ correction. $C_{\mathrm{lat}}(T_i)$ was fitted to a continuous frequency distribution spectrum by

$$C_{\mathrm{lat}}(T_i) = \sum_{j=1}^{m} A_{ij} x_j \qquad (i = 1, 2, \ldots, n) \tag{6}$$

where A_{i1} and A_{i2} are the Debye heat-capacity functions, A_{i3}–A_{im} indicate the heat capacities arising from a constant frequency distribution spectrum, $G(\tilde{\nu}_j)$, over an internal of frequency and x_j is the degree of freedom which is represented by

$$x_j = G(\tilde{\nu}_j)\, \Delta\tilde{\nu}_j \tag{7}$$

Equation (6) can be rewritten in a matrix form

$$\mathbf{C} = \mathbf{A}\mathbf{X} \tag{8}$$

where

$$\mathbf{C} = \begin{bmatrix} C(T_1) \\ C(T_2) \\ \vdots \\ C(T_n) \end{bmatrix}, \; A = \begin{bmatrix} A_{11}, & A_{12}, & \cdots & , A_{1m} \\ A_{21}, & A_{22}, & \cdots & , A_{2m} \\ \vdots & \vdots & & \vdots \\ A_{n1}, & A_{n2}, & \cdots & , A_{nm} \end{bmatrix}, \; \mathbf{X} = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_m \end{bmatrix} \tag{9}$$

The vector **X** can be determined by the least squares method

$$\mathbf{X} = (\tilde{\mathbf{A}}\mathbf{A})^{-1}(\tilde{\mathbf{A}}\mathbf{C}) \tag{10}$$

where $\tilde{\mathbf{A}}$ is the transposed matrix of **A**. For the actual calculation, the weighed least squares method was used, that is each matrix element A_{ij} was divided by the heat capacity $C_{\text{lat}}(T_i)$. The matrix having the elements $[A_{ij}/C_{\text{lat}}(T_i)]$ was designated as **B**. In this case, the vector **X** was determined by the equation

$$\mathbf{X} = (\tilde{\mathbf{B}}\mathbf{B})^{-1}(\tilde{\mathbf{B}}\mathbf{I}), \tag{11}$$

where **I** is unit matrix. The present parameters for the determination of the $\{x_j\}$ are two Debye frequencies ($\tilde{\nu}_{\text{D1}}$ and $\tilde{\nu}_{\text{D2}}$) included in A_{i1} and A_{i2}, the number of terms m in eqn. (6) and the cut-off frequency of the continuous spectrum ($\tilde{\nu}_{\text{cut}}$).

While keeping $m = 5$ and $\tilde{\nu}_{\text{cut}} = 700\ \text{cm}^{-1}$, the adjustable parameters $\tilde{\nu}_{\text{D1}}$ and $\tilde{\nu}_{\text{D2}}$ were varied by steps of $10\ \text{cm}^{-1}$. The "best" fit was found for the set of the parameters $\tilde{\nu}_{\text{D1}} = 130\ \text{cm}^{-1}$ and $\tilde{\nu}_{\text{D2}} = 180\ \text{cm}^{-1}$. The areas under

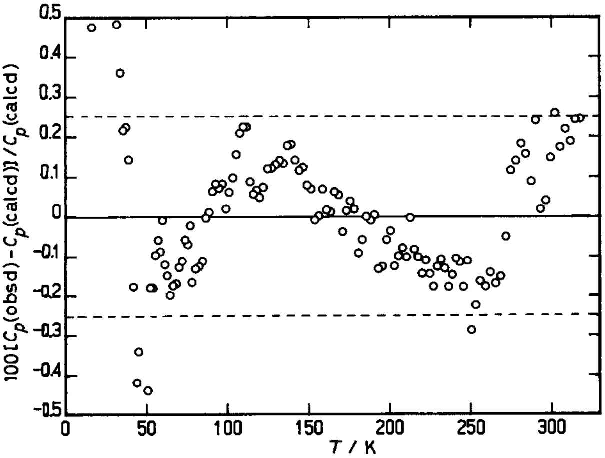

Fig. 3. Per cent deviation of the observed heat capacity of α-LiIO$_3$ from the fitting curve.

the respective frequency divisions in the plot of the effective frequency spectrum thus determined were 3.20, 0.80, 4.71, 0.11, and 0.94 in the range 0–130, 130–180, 180–353, 353–527, and 527–700 cm^{-1}, respectively. The total area under this frequency spectrum amounted to 9.76. The sum of 9.76 and six degrees of freedom arising from the intramolecular vibrations amounts to 15.76, which is somewhat larger than the value of 15 theoreti-

TABLE 2

Standard thermodynamic functions of α-$LiIO_3$ crystal ($J\ K^{-1}\ mol^{-1}$)

T/K	C_p°	$S^\circ(T) - S^\circ(0)$	$[H^\circ(T) - H^\circ(0)]/T$	$-[G^\circ(T) - H^\circ(0)]/T$
5	0.043	0.014	0.011	0.004
10	0.346	0.115	0.087	0.029
15	1.163	0.389	0.292	0.097
20	2.727	0.912	0.686	0.226
30	7.416	2.853	2.110	0.743
40	12.967	5.731	4.114	1.617
50	18.412	9.208	6.428	2.780
60	23.995	13.062	8.895	4.168
70	29.376	17.164	11.435	5.728
80	34.694	21.437	14.014	7.423
90	39.933	25.826	16.602	9.224
100	44.890	30.294	19.188	11.106
110	49.695	34.800	21.746	13.054
120	54.037	39.311	24.256	15.055
130	58.228	43.804	26.712	17.093
140	62.133	48.264	29.103	19.161
150	65.697	52.674	31.425	21.249
160	69.064	57.022	33.672	23.350
170	72.211	61.305	35.848	25.457
180	75.138	65.517	37.952	27.565
190	77.970	69.656	39.984	29.672
200	80.558	73.719	41.947	31.773
210	82.980	77.708	43.843	33.865
220	85.263	81.623	45.676	35.947
230	87.461	85.462	47.445	38.017
240	89.514	89.228	49.155	40.074
250	91.355	92.921	50.808	42.113
260	93.239	96.541	52.405	44.136
270	95.012	100.093	53.949	46.144
280	96.907	103.585	55.451	48.134
290	98.496	107.011	56.907	50.104
300	99.896	110.371	58.314	52.057
310	101.306	113.671	59.679	53.992
320	102.706	116.910	61.004	55.896
273.15	95.653	101.199	54.426	46.772
298.15	99.568	109.755	58.056	51.698

cally expected as the degrees of freedom for the $LiIO_3$ molecule in the absence of the $(C_p - C_v)$ term.

By combining this effective frequency spectrum and the six intramolecular vibrations given by eqn. (4), the observed C_p values were able to be well reproduced within the root-mean-square deviation of only ± 0.095 J K^{-1} mol^{-1} over the temperature region from 13 to 320 K. As shown in Fig. 3, deviation of the observed C_p values from the calculated values was within $\pm 0.25\%$ of the observed C_p values except for low-temperature regions, say below ~ 50 K.

Thermodynamic functions

In order to derive the thermodynamic quantities of the present compound over the temperature range from 0 to 320 K by the use of heat capacity data, the heat capacity values below 13 K were estimated by extrapolation of the fitted C_p curve down to 0 K. The standard molar enthalpy and entropy of the α-$LiIO_3$ crystal were determined by integration of the heat capacity with respect to T and $\ln T$, respectively. The standard thermodynamic functions of the present crystal thus obtained are given in Table 2 at selected temperatures from 0 to 320 K.

Single crystals of α-$LiIO_3$ show no optically induced damage and remain stable up to 256 °C, at which a phase transition occurs [3]. In order to throw light on this phase transition from a thermodynamic standpoint, heat capacity measurements in the range from 320 to 600 K are now being performed by use of a high-temperature adiabatic calorimeter [13].

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