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HEAT CAPACITY OF $LiInTe_2$

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The heat capacity of $LiInTe_2$ at constant pressure was measured with an adiabatic vacuum calorimeter in the temperature range $T = 7–300$ K. The standard molar enthalpy $H^o_m - H^o_m(0)$ and the standard molar entropy $S^o(T)$ were calculated. From a theoretical analysis, the contribution to the heat capacity due to the lattice anharmonicity was estimated. The increased effect of the lattice anharmonicity in $LiInTe_2$ is caused by specific properties of the Li-Te bond.

The ternary compound $LiInTe_2$ was recently synthesized, and a detailed structural analysis, the infrared lattice vibration spectra and heat capacity measurements in the temperature range from 250 to 500 K were reported [1–3]. In the present work, the heat capacity C_p of $LiInTe_2$ was measured in the temperature range from 7.1 to 311.0 K, and the experimental data were used to calculate the standard enthalpies and entropies and to determine the spectral moments of the phonon density states of the compound. Furthermore, an estimate of the contribution of the lattice anharmonicity to the heat capacity is given.

Experimental

The samples used in the experiment were prepared by direct fusion of stoichiometric mixtures of the elements, as described in detail in [1,2]. The heat capacity was measured with an adiabatic vacuum calorimeter, with an accuracy of 0.5% between 7 and 20 K, of 0.3% between 20 and 80 K, and 0.1% between 80 and 300 K (for the experimental details, see [4]). The resulting heat capacities are given in Table 1. On the basis of these data, we have calculated smoothed values for C_p, the standard molar enthalpy $H^o_m(T)–H^o_m(0)$ and the standard molar entropy $S^o_m(T)$ at $p = 101325$ Pa for the temperature range $T = 7–300$ K and by including the data from [3] up to 550 K. The results of these calculations are given in Table 2. For $T_o = 298.15$ K, we find $C_o(T_o) = 101.73$ J/mol deg, $H^o_m(T_o)–H_m(0) = 21.757$ kJ/mol and $S^o_m(T_o) = 168.10$ J/mol deg.

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Table 1 Experimental result for the heat capacity of $LiInTe_2$

T, K	C_p, J/mol deg	T, K	C_p, J/mol deg	T, K	C_p, J/mol deg
7.13	1.501	52.91	44.6	170.3	88.2
8.48	2.316	57.06	47.3	176.7	89.2
8.89	2.550	62.33	50.5	183.3	90.3
9.33	2.90	67.28	53.4	189.8	91.2
10.06	3.68	71.84	55.7	196.3	91.9
10.42	3.98	76.03	57.6	202.7	92.9
11.42	5.11	80.01	60.1	209.0	93.7
11.84	5.68	83.78	61.8	214.8	94.6
12.71	6.86	87.40	63.4	221.0	94.9
13.96	8.51	90.89	65.1	227.2	95.8
14.32	9.03	92.56	66.1	233.3	96.4
15.45	10.43	95.94	67.5	239.4	97.1
16.66	11.99	99.70	68.9	245.5	97.7
17.70	13.33	104.5	70.8	251.5	98.2
18.63	14.50	110.2	72.7	257.5	98.7
19.65	15.78	115.7	74.6	263.5	99.1
20.92	17.33	121.0	76.1	269.4	99.7
23.06	19.79	126.2	77.9	275.3	100.1
25.58	22.56	131.3	79.3	281.2	100.5
28.56	25.40	136.3	80.8	287.0	101.0
31.80	28.66	141.2	82.0	293.3	101.4
34.91	31.28	146.0	83.1	299.6	101.8
38.51	34.0	150.8	84.3	305.3	102.3
42.08	36.9	155.5	85.3	311.0	102.6
46.18	39.8	160.1	86.0		
49.72	42.1	164.7	87.2		

Results and discussion

To determine the first even moment of the vibrational spectrum, we use the relation

$$\theta_D^2(T) = \theta_\infty^2 \left\{ 1 - A\,\frac{\theta_o^2}{T^2} + B\,\frac{\theta_o^4}{T^4} \right\} \tag{1}$$

for the temperature-dependence of the equivalent Debye temperature θ_D in the quasiharmonic approximation, which is valid in the temperature range $T > \theta_D/2\pi$ [5]. The Debye temperature θ_∞ for the high-temperature limit $T \to \infty$, and the coefficients A and B in Eq. (1) are given by

Table 2 Smoothed values for C_p, the standard molar enthalphy and the standard molar entropy of LiInTe$_2$

T, K	C_p, J/mol deg	$H_m(T) - H_m(0)$, J/mol	$S_m(T)$, J/deg mol
7	1.441	3.9700	0.8620
10	3.560	11.063	1.6831
15	9.869	44.095	4.2738
20	16.210	109.39	7.9871
30	26.898	332.63	16.852
40	35.289	639.92	25.610
50	42.474	1029.4	34.273
60	49.143	1488.1	42.615
80	59.860	2581.5	58.270
100	69.086	3874.9	72.661
150	84.070	7734.6	103.75
200	92.551	12171	129.22
250	98.083	16944	150.50
300	101.86	21946	168.73
350	105.54	27137	184.73
400	108.70	32494	199.03
450	111.65	38003	212.00
500	114.48	43657	223.91
550	117.22	49450	234.96

$$\theta_\infty = \frac{h}{k}\left(\frac{5\mu_2}{3}\right)^{\frac{1}{2}}, A = \frac{3}{100}\left(\frac{\mu_4}{\mu_2^2} - \frac{25}{21}\right),$$

$$B = \frac{1}{1400}\left(\frac{\mu_6}{\mu_2^3} - \frac{125}{81} - 100A\right) \qquad (2)$$

where μ_2, μ_4 and μ_6 are the first even moments of the vibrational spectrum. To evalute μ_i by means of Eqs (1) and (2), we have calculated the apparent Debye temperature θ_D from the heat capacities in Table 1, and Fig. 1 shows a plot of θ_D^3 against $1/T^2$ for the temperature range $T > 40$ K. We see that θ_D increases up to about 100 K. At $T > 100$ K, a rapid decrease of θ_D sets in due to lattice anharmonicity effects [5]. Then, assuming that the lattice anharmonicity can be neglected at $T < 100$ K, relation (1) was fitted to the data points of Fig. 1. The spectral moments obtained in this manner are $\mu_2 = 2.45 \cdot 10^{25} s^{-2}$, $\mu_4 = 1.07 \cdot 10^{51} s^{-4}$ and $\mu_6 = 5.15 \cdot 10^{76} s^{-6}$. For the high-temperature limit of the Debye temperature, we find $\theta_\infty = 306.8$ K. Using these values for μ_1 and θ_∞, we can calculate the equivalent Debye temperature θ_D by means of Eq. (1) for the temperature range $T > 100$ K,

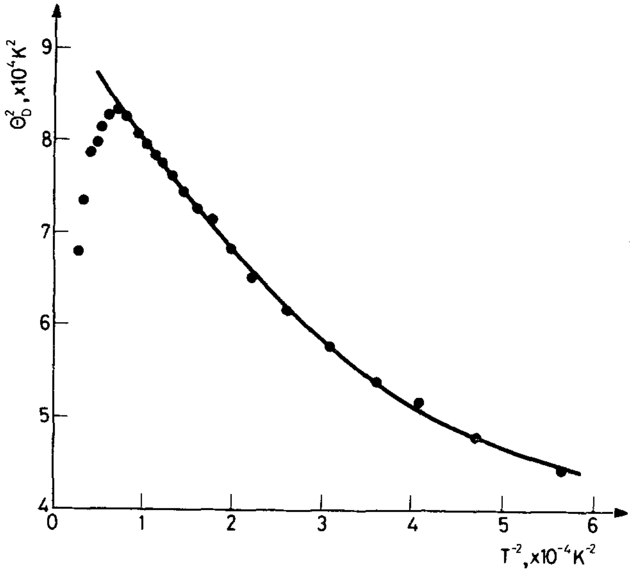

Fig. 1 Plot of Θ_D^2 against $1/T^2$ (● – experimental points, the full curve is calculated with relation (1))

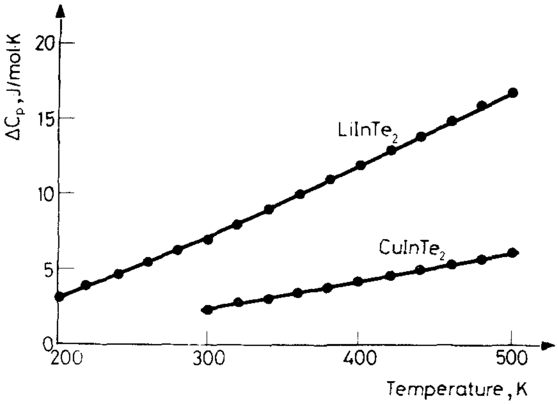

Fig. 2 Anharmonic contribution to the heat capacity in $LiInTe_2$ and $CuInTe_2$

and then evaluate the harmonic part of the heat capacity C_{ph}. Then, the difference $\Delta C_p = C_{p.\mathrm{exp}} - C_{ph}$ represents the contribution to the heat capacity due to lattice anharmonicity. With the heat capacities from Table 1 for $T = 180$ to 310 K, and from [3] for the temperatures above 300 K, we find the $\Delta C_p(T)$ curve shown in Fig. 2. For comparison, the estimated anharmonic contribution ΔC_p to the heat capacity of $CuInTe_2$ [6] is shown in Fig. 2, too. It is obvious that, in agreement with previous estimates [3], the influence of the lattice anharmonicity on the heat capacity is more pronounced in $LiInTe_2$ than in $CuInTe_2$. Since both $LiInTe_2$ and $CuInTe_2$ crystallize in the chalcopyrite structure, and since the properties of the In-Te bond are expected to be the same in the two compounds, we conclude that the increased effect of lattice anharmonicity on the heat capacity in $LiInTe_2$ is due to specific properties of the Li-Te bond.

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Zusammenfassung – Die Wärmekapazität von $LiInTe_2$ bei konstantem Druck wurde mit einem adiabatischen Vakuumkalorimeter im Temperaturbereich $7 \leqslant T \leqslant 300$ K bestimmt. Die molare Standardenthalpie $H^o_m - H^o_m(0)$ und die molare Standardentropie $S^o(T)$ wurden berechnet. Aus einer theoretischen Analys wurde der Anteil der Gitteranharmonizität an der Wärmekapazität abgeschätzt. Der erhöhte Einfluss der Gitteranharmonitität in $LiInTe_2$ wird durch spezifische Eigenschaften der Li-Te-Bindung verursacht

РЕЗЮМЕ — С помощью адиабатического вакуумного калориметра измерена в области температур 7—300 К и при постоянном давлении теплоемкость $LiInTe_2$. Вычислена стандартная молярная энтальпия $H^0_M - H^0_M(0)$ и стандартная молярная энтропия $S^0(T)$. На основе теоретического анализа установлен вклад решеточной ангармоничности в теплоемкость. Значительный вклад решеточной ангармоничности в $LiInTe_2$ обусловлен специфическими свойствами связи Li—Te.