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Heat Capacity and Thermodynamic Properties of Tl_2Te at Low Temperatures

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Among a number of Tl_2X (X = S, Se, Te)-type thallium chalcogenides the heat capacities of Tl_2Se and Tl_2S compounds have been studied and their thermodynamic parameters calculated /1, 2/. However, for Tl_2Te such data is lacking. The aim of the present investigation is to study the heat capacity of Tl_2Te and to calculate its thermodynamic parameters, as well as to interpret the resultant data on the low-temperature heat capacity in the light of heat-capacity theories of solids.

It should be noted that there is ambiguous information on the existence of a phase with composition Tl_2Te in the Tl-Te equilibrium diagram. For example, elsewhere /3, 4/ some physico-chemical and semiconductive properties of Tl_2Te compounds have been obtained, whereas the authors of another report /5/ doubt as to the existence of a Tl_2Te compound in the Tl-Te diagram.

Specimens were synthetized by fusing the components in equimolar ratios (2:1) in evacuated quartz ampoules. In doing so, the components used to produce the specimens had a purity of 99.99%. The crystals obtained in this way were subjected to physico-chemical and X-ray analyses. The small Tl_2Te crystals proved to be of single-phase nature and had p-type conductivity with a resistivity of 20 Ωm, a density of 54×10^3 kg/m^3, a microhardness of 52×10^7 N/m^2, and a melting point of 415 ^oC.

The crystals belonged to the rhombic system with the lattice parameters a = 0.892 nm and c = 1.263 nm (all the data were obtained at T ≈ 300 K), which is in satisfactory agreement with published data /6, 7/.

Heat-capacity measurements were conducted with the aid of a low-temperature adiabatic calorimetric unit operating under pulsed conditions and used

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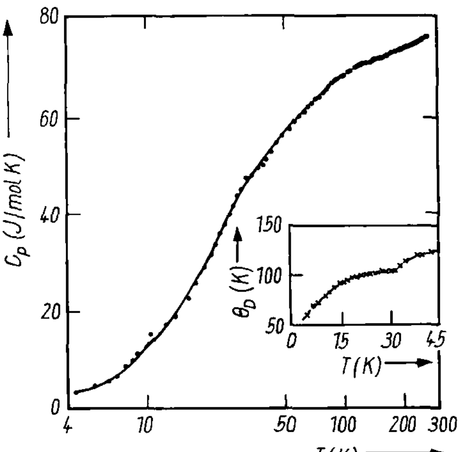

Fig. 1. Temperature dependence of the heat capacity of Tl_2Te in the temperature range from 4.32 to 299.39 K (semi-logarithmic scale)

earlier /2, 8, 9/. Below 20 K the temperature of the calorimetric system was measured by means of a germanium resistance thermometer, whereas above 20 K it was measured with a TSPI-2B-type platinum resistance thermometer. The Tl_2Te specimens with a mass of 0.11119 mol, placed into the calorimeter, looked like small crystals with linear sizes of ≈ 2 to 3 mm.

The heat capacity of the empty calorimeter was measured separately and amounted to no more than 30% of the total heat capacity of the calorimetric system. 110 values of Tl_2Te heat capacity were obtained in the temperature range from 4.32 to 299.39 K; the measurement results are depicted in Fig. 1, whereas the rectified heat-capacity values are presented in Table 1. In this case the experimental error is from 2 to 3% at the lower measurement limit, whereas above 10 K it amounts to no more than 0.3%.

The Θ_D/T dependence for Tl_2Te, that grows monotonically with temperature (see inset in Fig. 1), has been determined with the use of the results of calorimctric measurements on the basis of the standard Debye dependence for the heat capacity $C_v = f(\Theta_D/T)$ in the range from 5 to 40 K. This suggests that the phonon spectrum of Tl_2Te is a non-Debye spectrum and exhibits a more complex nature. At ≈ 50 K the $C_p(T)$ curve goes beyond the scope of the Dulong and Petit law. A high heat-capacity value in the room-temperature region is typical of all the thallium chalcogenides studied /1, 2, 10/ and is likely to bear witness to a high anharmonicity of the thermal vibrations of lattices in these compounds.

It has been established that the heat-capacity behaviour of Tl_2Te in the temperature range from 5 to 50 K is described satisfactorily by the equation /11, 12/

Table 1

Heat capacity, entropy, and variations in the enthalpy and the reduced Gibbs energy for Tl_2Te

T(K)	C_p (J/mol K)	S_T (J/mol K)	$H_T - H_o$ (J/mol)	$-\Delta G$ (J/mol K)
5	3.473	1.389	6.947	0
10	12.68	7.784	45.68	3.216
20	29.38	21.41	251.7	8.827
30	44.21	36.27	623.4	15.49
40	50.39	49.96	1111	22.44
50	55.66	61.77	1632	29.15
60	59.51	72.28	2208	35.48
70	62.33	81.67	2818	41.41
80	64.57	90.14	3453	46.98
90	66.30	97.84	4107	52.20
100	67.59	104.9	4777	57.11
110	68.67	111.4	5459	61.75
120	69.55	117.4	6150	66.13
130	70.24	122.9	6849	70.29
140	70.80	128.2	7554	74.24
150	71.27	133.1	8265	77.99
160	71.70	137.7	8979	81.58
170	72.11	142.0	9698	85.00
180	72.48	146.2	10421	88.29
190	72.78	150.1	11148	91.45
200	73.06	153.8	11877	94.47
210	73.40	157.4	12609	97.39
220	73.82	160.8	13345	100.2
230	74.26	164.1	14086	102.9
240	74.62	167.3	14830	105.5
250	74.99	170.3	15579	108.0
260	75.25	173.3	16330	110.5
270	75.42	176.1	17084	112.8
280	75.43	178.8	17989	114.6
298.15	75.45	183.6	19497	118.2
300	75.45	184.5	19799	118.6

$$C_{1,3} = D_1\left(\frac{\Theta_1}{T}\right) - \frac{\Theta_3}{\Theta_1}\left[D_1\left(\frac{\Theta_3}{T}\right) - D_3\left(\frac{\Theta_3}{T}\right)\right]. \qquad (1)$$

Here, Θ_1 = 157 K and Θ_3 = 47 K. The results of a comparison between the experimental heat-capacity values of Tl_2Te and those calculated with (1) are given in Fig. 2.

On the basis of precision calorimetric measurements the thermodynamic parameters of Tl_2Te have been calculated. The entropy (S_T), and variations

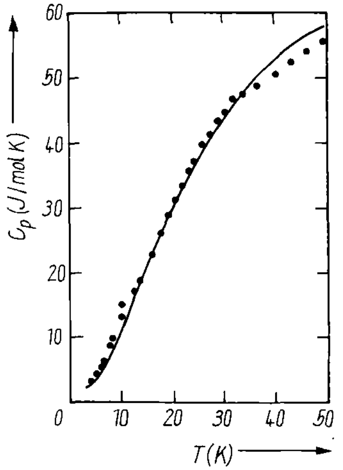

Fig. 2. Comparison between experimental heat-capacity values of Tl_2Te (points) and the values calculated (solid line) with (1)

in the enthalpy ($H_T - H_o$) and the reduced Gibbs energy (ΔG) have been calculated with the following relationships:

$$S_T = \int_0^T C_p(T)/T \, dT \ , \tag{2}$$

$$H_T - H_o = \int_0^T C_p(T) \, dT \ , \tag{3}$$

$$\Delta G = - \left[S_T - \frac{(H_T - H_o)}{T} \right] \ . \tag{4}$$

The results of calculations of the thermodynamic parameters of Tl_2Te are presented in Table 1, too. The values of these quantities under standard conditions (T = 298.15 K) proved to be S_T = 183.6 J/mol K, $H_T - H_o$ = 19497 J/mol, and $-\Delta G$ = 118.2 J/molK.

Elsewhere /13/ S^o_{293} = 185.4 J/mol K has been obtained by the method of comparative calculations, for materials of the same type, which is in good agreement with the results of our experiment. Other investigators /7/ used the e.m.f. method to determine the entropy value of Tl_2Te amounting to S^o_{298} = 197.9 J/molK, which is higher than our result by ≈ 8%.

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