Thermochimica Acta, 43 (1981) 297—303
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

HEAT CAPACITY MEASUREMENTS OF SnSe AND $SnSe_2$

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(Received 28 July 1980)

ABSTRACT

The heat capacities of SnSe and $SnSe_2$ were measured in the temperature range 230—580 K using a computer interfaced differential scanning calorimeter. From these measurements, the Debye temperatures of SnSe and $SnSe_2$ were calculated as a function of temperature. An estimated Debye temperature of 220 K for SnSe was used to calculate the absolute entropy of SnSe at 298 K to be 85.2 ± 6.0 J K^{-1} $mole^{-1}$. In the light of other work, the suitability of Debye temperatures for estimating low temperature heat capacities of $SnSe_2$ is questioned.

INTRODUCTION

This work represents part of a series of investigations to establish the thermodynamic properties of Group IV chalcogenides [1,2]. In particular, the independent confirmation of the absolute entropy of these materials is important for the evaluation of transport studies on these systems. Heat capacities for SnSe have been reported only at higher temperatures (300—787 K) [3]. No such data are available for $SnSe_2$. The present work is concerned with heat capacity measurements of SnSe and $SnSe_2$ in the temperature range 230—580 K. These data are used to calculate the thermodynamic functions of SnSe and $SnSe_2$.

EXPERIMENTAL PROCEDURES

Heat capacity measurements

A differential scanning calorimeter (Perkin-Elmer DSC-2) was used for the thermal analysis of all samples. An enclosed, air cooled refrigeration unit (Perkin-Elmer Intracooler II) was attached to the DSC allowing heat capacity measurements down to 220 K. The DSC output was changed into digital form through the use of an analog/digital converter (Perkin-Elmer Digital Data Recorder). The digital output was recorded on paper punch tape (Iomec Inc.). The range of the digital output is 0—10 000 digital units which corresponds to full-scale displacement of the DSC recorder. The output was sampled in 1.2 s intervals.

The heat capacity calculations from the recorded digital amplitudes were performed on a Hewlett-Packard 9821A programmable calculator. The DSC output on tape was read by an optical tape reader (Hewlett Packard 2748B) and assimilated into the calculator. Heat capacities were calculated in 10 K intervals. For each calculation, amplitudes obtained from baseline, standard and sample scans are recorded from 5 K below to 5 K above the temperature at which the heat capacity is measured. A linear least-squares treatment is performed on the amplitudes and a "fitted" amplitude is calculated at the mean temperature of the measurements. These uncorrected displacements are calculated at every 10 K for baseline, sample and standard scans. Corrected standard and sample amplitudes are obtained by subtracting the uncorrected standard and sample displacements at each temperature and accounting for the amplitude differences due to the difference in pan weights. Further details of the data treatment have been reported earlier [4].

Sample preparation and pan loading procedures

Samples of SnSe and $SnSe_2$ were prepared by different methods. SnSe was synthesized by sealing stoichiometric quantities of the elements (99.999%) into previously cleaned and outgassed fused silica ampoules at a pressure of 10^{-4} Pa [5]. The starting mixture was annealed at 1023 K for about 24 h and then sublimed repeatedly in a 973—823 K temperature gradient. Debye—Scherrer X-ray diffraction powder patterns could be indexed on the basis of the orthorhombic unit cell of SnSe and the calculated lattice parameters ($a = 4.450 \pm 0.007$ Å, $b = 11.504 \pm 0.019$ Å, $c = 4.146 \pm 0.007$ Å) are in good agreement with literature values ($a = 4.445$ Å, $b = 11.501$ Å, $c = 4.153$ Å) [6].

$SnSe_2$ was prepared by annealing stoichiometric amounts of SnSe and Se at 473 K for about 300 h in sealed evacuated fused silica ampoules. The annealing product was then chemically transported with iodine in a different evacuated closed ampoule of fused silica (similar to procedures described elsewhere [7]) in a temperature gradient 593—693 K with the source material at 593 K. Under these conditions $SnSe_2$ is transported to the higher temperature, where it is deposited in the form of single crystal platelets [8]. Debye—Scherrer X-ray patterns of the powdered crystals could be indexed on the basis of the hexagonal structure of $SnSe_2$ and the calculated lattice parameters ($a = 3.806 \pm 0.005$ Å, $c = 6.149 \pm 0.008$ Å) are in agreement with literature values ($a = 3.807$ Å, $c = 6.128$ Å) [9].

Prior to loading the calorimeter, SnSe and $SnSe_2$ powders were outgassed at a temperature of about 423 K at a pressure of 10^{-4} Pa. To determine whether these materials react with the aluminum sample pans, SnSe and $SnSe_2$, respectively, were sealed under dry nitrogen atmosphere in aluminum pans and heated at 873 K for 4 h. The mass of the pans remained constant within error limits (±0.02 mg). Microscopic examination of the pans revealed no visible reaction between the samples and the aluminum.

All samples were loaded and hermetically sealed in aluminum pans in a dry box under nitrogen atmosphere. The masses of the powdered samples and aluminum pans were determined using a Cahn microbalance.

Experimental conditions

The temperature range for the heat capacity measurements was 230—580 K. Sample masses of 30—45 mg were used. The heat capacity data were obtained in intervals of 40—60 K using a heating rate of 20 K min^{-1} and a range sensitivity of 21 mJ s^{-1}.

Sapphire (Perkin-Elmer 219-036) was used as the heat capacity standard. The temperature scale was calibrated using various standards as described earlier [10]. The accuracy of the recorded temperature is estimated to be ±0.2 K and that of the heat capacity measurement is estimated to be better than ±1% [4].

RESULTS

The heat capacity of SnSe

The heat capacity of SnSe was measured in the temperature range 230—580 K and is graphically represented in Fig. 1. A least-squares analysis of the data yields the equation

$$C_p = 49.06 + 1.25 \times 10^{-2}T - 9.15 \times 10^{4}T^{-2} \ (\text{J K}^{-1} \text{ mole}^{-1}) \qquad (1)$$

The standard deviation of the experimental data from eqn. (1) is ±0.460 J K^{-1} mole^{-1} and the root mean square deviation is ±0.8%. Also shown in Fig. 1 are the heat capacity data from earlier measurements [3]. At high temperatures, the literature values are about 4% higher than those of the present work which is well outside present error limits. This discrepancy could be due to difficulties encountered with the isoperibolic metalblock-drop-calorimeter [11] used in the earlier experiments [3].

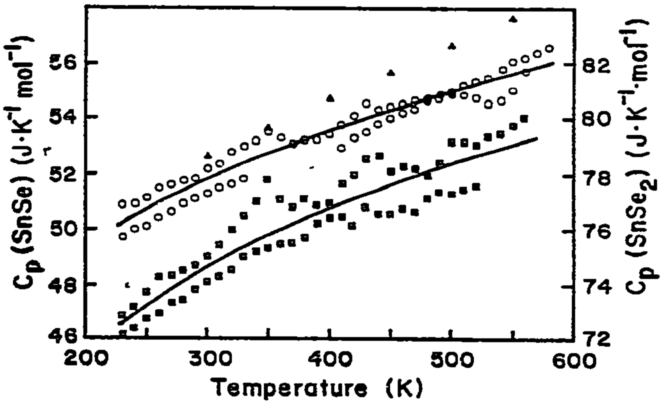

Fig. 1. Heat capacities of SnSe and $SnSe_2$ as a function of temperature. The solid lines represent the result of a least-squares treatment of the experimental data. (○ SnSe, this work; ▲ SnSe, ref. 3; ■ $SnSe_2$, this work.)

The heat capacity of $SnSe_2$

The heat capacity of $SnSe_2$ was measured in the temperature range 230—570 K. The data are shown in Fig. 1. A least-squares analysis of the data yields the equation

$$C_p = 73.39 + 1.15 \times 10^{-2}T - 1.92 \times 10^5 T^{-2} \text{ (J K}^{-1}\text{ mole}^{-1}\text{)} \qquad (2)$$

The standard deviation of the experimental data from eqn. (2) is ±0.807 J K^{-1} $mole^{-1}$ and the root mean square deviation is ±1.0%.

DISCUSSION

Calculation of the absolute thermodynamic functions $(H_T^0 - H_0^0)$, S_T^0 and $(G_T^0 - H_0^0)$ requires that the heat capacity be known from 0 K. Since the present measurements are limited to temperatures above 230 K, it was necessary to extrapolate the high temperature heat capacity to low temperatures. The most common method of extrapolation of high temperature heat capacities of solids involves the use of the three-dimensional Debye function [12]

$$C_v = 3\mathrm{R} \cdot D(\theta_D/T) \qquad (3)$$

where

$$D(\theta_D/T) = 12\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1} - \frac{3\theta_D/T}{e^{(\theta_D/T)} - 1} \qquad (4)$$

and θ_D is the Debye temperature defined as

$$\theta_D = h\nu/k \qquad (5)$$

In eqn. (5) h is Planck's constant, k is the Boltzmann constant and ν is the vibrational frequency. For binary and ternary compounds, eqn. (3) becomes

$$C_v = 6R \cdot D(\theta_D/T) \text{ (binary)} \qquad (6)$$

and

$$C_v = 9R \cdot D(\theta_D/T) \text{ (ternary)} \qquad (7)$$

Also, since the heat capacity is measured as C_p, C_v must first be calculated. Since no compressibility data are available for these compounds, the Nernst—Lindemann approximation [13] is used for these calculations. The difference between C_p and C_v is given by the expression

$$C_p - C_v = A_0 C_p^2 T/T_m \qquad (8)$$

where T_m is the melting temperature (1134 K for SnSe and 948 K for $SnSe_2$) and A_0 is a universal atomic constant 5.12×10^{-3} J^{-1} K mole. For diatomic and triatomic solids such as SnSe and $SnSe_2$, C_p in eqn. (8) must be expressed per atom. With the calculated ratio $C_v/6R$ (or $C_v/9R$) for SnSe (or $SnSe_2$) as a function of temperature, θ_D/T can be obtained from tables calculated by Beattie [14]. Values for θ_D vs. T are plotted in Fig. 2 for SnSe and $SnSe_2$.

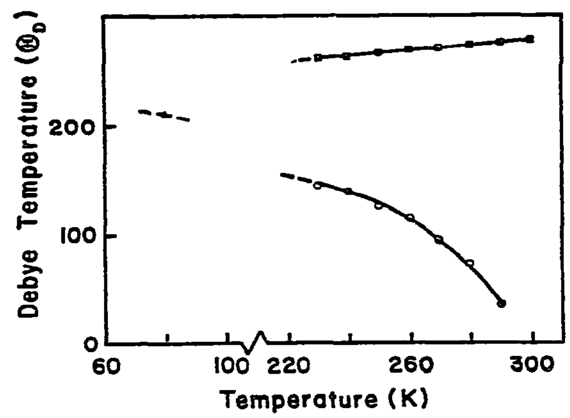

Fig. 2. Variation of the Debye temperature (calculated from C_v) with temperature. (○ SnSe, this work; ▲ SnSe, ref. 15; ■ $SnSe_2$, this work.)

A single data point available for SnSe at 80 K [15] allows sufficient extension of the curve in Fig. 2 to reveal that θ_D does not remain constant over the intermediate temperature range, but increases steadily. As an approximation, eqn. (6) was used with a θ_D value of 220 K to extrapolate the values of

TABLE 1

Calculated thermodynamic parameters for SnSe(s)

T (K)	C_p ($J\,K^{-1}\,mole^{-1}$)	$(H_T^\circ - H_0^\circ)$ ($J\,mole^{-1}$)	S_T° ($J\,K^{-1}\,mole^{-1}$)	$-(G_T^\circ - H_0^\circ)$ ($J\,mole^{-1}$)
0.0	0.00	0.00	0.00	0.00
20.0	2.88	18.10	1.09	3.70
40.0	18.15	208.7	6.93	68.40
60.0	27.85	662.1	15.99	297.0
80.0	35.53	1301	25.13	709.1
100.0	40.35	2062	33.62	1298
120.0	43.42	2902	41.26	2049
140.0	45.52	3792	48.13	2945
160.0	47.04	4717	54.30	3971
180.0	48.03	5669	59.91	5114
200.0	49.13	6641	65.03	6365
220.0	49.65	7630	69.75	7714
240.0	50.46	8633	74.11	9153
260.0	50.95	9647	78.17	10677
280.0	51.38	10670	81.96	12279
298.15	51.76	11606	85.20	13796
300.0	51.78	11702	85.52	13954
340.0	52.51	13788	92.05	17508
380.0	53.16	15902	97.93	21310
420.0	53.78	18041	103.3	25336
460.0	54.36	20204	108.2	29567
500.0	54.93	22389	112.8	33987
540.0	55.48	24597	117.0	38584
580.0	56.02	26827	121.0	43344

TABLE 2

Calculated thermodynamic parameters for $SnSe_2(s)$

T (K)	C_p ($J\ K^{-1}\ mole^{-1}$)	$(H^\circ_T - H^\circ_{230})$ ($J\ mole^{-1}$)	S°_{230} ($J\ K^{-1}\ mole^{-1}$)	$-(G^\circ_T - H^\circ_{230})$ ($J\ mole^{-1}$)
230.0	72.41	0.00	0.00	0.00
270.0	73.81	2927	11.73	240.8
298.15	74.66	5018	19.10	676.7
310.0	74.97	5904	22.02	920.5
350.0	75.86	8921	31.17	1988
390.0	76 62	11971	39.42	3403
430.0	77.31	15050	46.94	5133
470.0	77.94	18155	53.84	7150
510.0	78.53	21285	60.23	9434
550.0	79.09	24437	66.18	11963

C_p from 220 K to 0 K. These data are given in Table 1 along with values for the thermodynamic parameters $(H^\circ_T - H^\circ_0)$, S°_T and $-(G^\circ_T - H^\circ_0)$ which are calculated by numerically integrating the heat capacities from 0 K to 580 K. Heat capacities above 220 K are from eqn. (1). The absolute entropy, enthalpy and Gibbs free energy determined are $S^\circ_{298} = 85.2 \pm 6.0\ J\ K^{-1}\ mole^{-1}$, $H^\circ_{298} - H^\circ_0 = 11.6 \pm 1.0\ kJ\ mole^{-1}$ and $G^\circ_{298} - H^\circ_0 = -13.8 \pm 2.0\ kJ\ mole^{-1}$. The absolute entropy based on present heat capacity data agrees with the value of $90.6 \pm 5.0\ J\ K^{-1}\ mole^{-1}$ obtained from a second-law analysis of Knudsen effusion data of SnSe [8]. Mills' [16] value of $89.5 \pm 6.3\ J\ K^{-1}\ mole^{-1}$, which was determined by an extension of the Latimer additivity method, is also in agreement with our result. Latimer's method of estimating entropies involves the addition of entropy contributions from the cation and anion of the material [17].

Figure 2 shows that the calculated θ_D for $SnSe_2$ remains fairly constant for the temperature range 230—300 K. Studies of other Group IV dichalcogenides, however. have shown [18] that below 200 K, θ_D decreases rapidly. In the absence of any low temperature heat capacity data, it is not possible to make an approximation of θ_D. The calculation of the thermodynamic parameters was thus done from 230 K rather than from 0 K. The results are listed in Table 2. Estimates of the absolute entropy of $SnSe_2$ have been made by comparison with SnS_2 [16]. This comparison yields a value of $112.6 \pm 6.0\ J\ K^{-1}\ mole^{-1}$ which is in agreement with the second-law analysis of Knudsen effusion studies of $SnSe_2$ [8] yielding a value of $105.4 \pm 6.0\ J\ K^{-1}\ mole^{-1}$.

ACKNOWLEDGEMENTS

The authors are pleased to acknowledge the support of this work in part by the National Aeronautics and Space Administration and by the National Science Foundation, Polymers Program (DMR 78-15279).

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