Thermochimica Acta, 27 (1978) 223–231

HEAT CAPACITY MEASUREMENTS OF GeS, GeSe AND GeTe

HERIBERT WIEDEMEIER, PAUL SIEMERS*, UMESH GAUR AND
BERNHARD WUNDERLICH

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181 (U.S.A.)
(Received 28 November 1977)

ABSTRACT

The heat capacities of GeS, GeSe and GeTe were measured in the temperature range 220–610 K, employing a computer interfaced differential scanning calorimeter. Using the measured heat capacity data, the Debye temperatures of GeS, GeSe and GeTe were estimated to be 360, 280 and 180 K, respectively. The IV–VI compounds with cubic structure have lower average force constants than the orthorhombic compounds. The absolute entropies at 298 K were calculated to be 59.4 ± 4.0, 71.6 ± 4.0 and 97.5 ± 4.0 J K^{-1} $mole^{-1}$ for GeS and GeTe, respectively.

INTRODUCTION

Crystal growth studies of GeS, GeSe and GeTe by chemical vapor transport made it necessary to discuss the thermodynamic functions of these compounds at various temperatures[1-3]. The heat capacities of GeS, GeSe and GeTe, however, had not been measured in the temperature region of interest. This paper presents such heat capacity data in the temperature range 220–610 K. The heat capacities are discussed in terms of the Debye theta temperatures and the crystal structures. In addition, the absolute entropies of the germanium monochalcogenides are calculated from the heat capacity data.

EXPERIMENTAL PROCEDURES

Heat capacity measurements

A differential scanning calorimeter (Perkin-Elmer DSC-2) was used for the thermal analysis of all samples. The DSC output was recorded in digital form, suitable for computer evaluation. A detailed description of the equipment and computer program is given elsewhere[4]. Data points were sampled every 1.2 s and averaged for heat capacity evaluation. Accuracies better than ± 0.5% have been

---

* Present address: General Electric Company, Schenectady, N.Y. (U.S.A.).

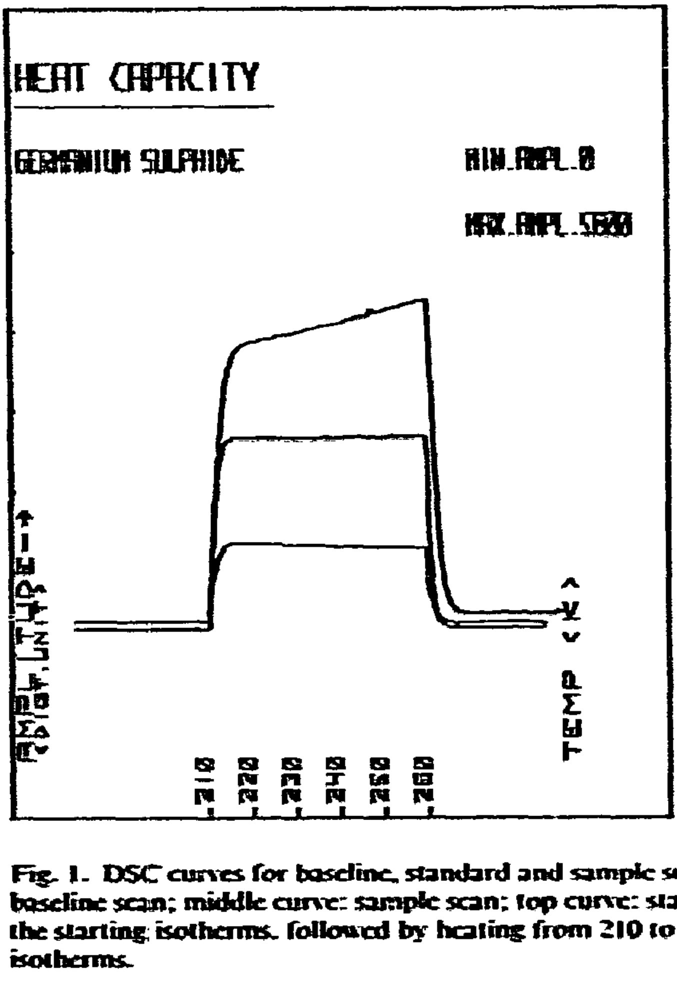

Fig. 1. DSC curves for baseline, standard and sample scans (print-out of data tapes). Lowest curve: baseline scan; middle curve: sample scan; top curve: standard scan (Al_2O_3). The left horizontals are the starting isotherms, followed by heating from 210 to 260 K. The right horizontals are the ending isotherms.

achieved on measurements with zinc[4]. Heating rates used in this work were 10 K min^{-1}. The sample masses varied from about 20 to 60 mg. The measurements were carried out under a flow of dry nitrogen. High purity sapphire crystals of well known heat capacity[5] were employed as standards. The temperature range of measurement was 220–610 K.

The raw data for a baseline, standard and sample scan consist of three regions as shown in Fig. 1. Heat capacities are calculated in 10 K intervals. For each calculation, 50 signal 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 50 signal amplitudes and a "fitted" amplitude is calculated at the mean temperature of the measurements. The extrapolated baseline amplitude is subtracted from the "fitted" signal amplitude to yield an uncorrected displacement. The uncorrected displacements are calculated every 10 K for baseline, sample and standard scans. Corrected standard and sample amplitudes are obtained by subtracting the uncorrected baseline displacements from the uncorrected standard and sample displacements at each temperature.

Sample preparation and pan loading procedures

The samples of GeS, GeSe and GeTe used for these studies were prepared from the elements by sealing stoichiometric quantities of Ge (99.999%) and the corresponding chalcogen (99.999%) in previously cleaned and outgassed[6] fused silica ampoules at a pressure of 10^{-4} Pa. The ampoule contents were annealed at 823 K for several hours and sublimed repeatedly and quantitatively in an 873 → 773 K temperature gradient. Debye-Scherrer X-ray diffraction photographs of the products yielded lattice parameters for the orthorhombic GeS ($a = 0.4303 \pm 0.0003$ nm, $b = 0.3652 \pm 0.0003$ nm, $c = 1.0449 \pm 0.0009$ nm), for the orthorhombic GeSe ($a = 0.4387 \pm 0.0006$ nm, $b = 0.3837 \pm 0.0006$ nm, $c = 1.083 \pm 0.0015$ nm) and for the rhombohedral GeTe ($a = 0.5982 \pm 0.0004$ nm and $\alpha = 88.22 \pm 0.2°$), in good agreement with the literature values. Further details of sample preparation and crystal structure are reported elsewhere[7, 8]. Prior to loading the samples into the aluminum pans, each compound was dried and outgassed at 475 K at a pressure of 10^{-4} Pa.

To determine whether these compounds react with aluminum, GeS, GeSe and GeTe, respectively, were sealed under an atmosphere of desiccated nitrogen in aluminum pans and heated at 823 K for 2 h. The mass of the sample plus pan remained constant after heating (within ± 0.02 mg). Microscopic examination (25×) of the opened pans revealed no visible reaction between the samples and the inside of the aluminum container.

For the actual heat capacity runs, all samples were loaded and hermetically sealed in aluminum pans in a dry box containing a nitrogen atmosphere. The mass of the powdered sample was determined by weighing the pan and cover before and after loading using a Cahn microbalance. The pans were filled and sealed to minimize the free volume containing nitrogen. At the end of each heat capacity run, the sample plus pan were weighed to confirm constant mass within experimental limits of error.

RESULTS

The heat capacity of GeS

The heat capacity of GeS was determined in the temperature range 220–610 K and is graphically represented in Fig. 2. A least-squares treatment of the data yielded the equation

$$C_p = 46.5 + 1.49 \times 10^{-2}\,T - 2.01 \times 10^{5}\,T^{-2}\ (\mathrm{J\,K^{-1}\,mole^{-1}}) \qquad (1)$$

which is valid in the temperature range 220–510 K. The heat capacity values for temperatures between 520–610 K were not included in the least-squares treatment. An exothermic thermal effect with an estimated heat of 105 J mole^{-1} was observed at these temperatures. The thermal effect started at 520 K, at which temperature previous X-ray diffraction studies revealed a halt in the expansion of the crystallographic *a*- and *b*- axes of GeS (about 513 K)[8]. Since the thermal effect is exothermic, stronger bonds may be formed during the structural changes[5] at these temperatures. A further interpretation of these effects and halt in the thermal expansion is not

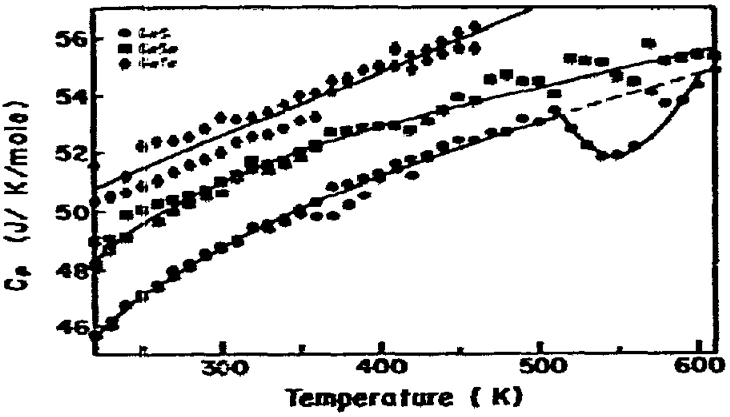

Fig. 2. The measured heat capacity values of GeS, GeSe and GeTe as a function of temperature. The least-squares fit heat capacity functions for GeS, GeSe and GeTe are represented as solid lines.

justified based on present data. The "fitted curve" represented by eqn. (1) is plotted in Fig. 2. The standard deviation of the data is ± 0.1 J K^{-1} mole^{-1}. The maximum deviation of the heat capacity values from eqn. (1) is ± 0.5%.

The heat capacity of GeSe

The heat capacity of GeSe was measured in the temperature range 220–610 K in three runs. The results are graphically represented in Fig. 2. A least-squares analysis of the data yielded the following heat capacity function of GeSe

$$C_p = 50.2 + 9.60 \times 10^{-3}\, T - 1.87 \times 10^{5}\, T^{-2}\ (\text{J K}^{-1}\ \text{mole}^{-1}) \tag{2}$$

which is also shown in Fig. 2. The maximum deviation of the heat capacity values from eqn. (2) is ± 1.5% and the standard deviation of the data is ± 0.4 J K^{-1} mole^{-1}. No unusual thermal effects were observed in the GeSe heat capacity data which is consistent with the thermal expansion studies[7].

The heat capacity of GeTe

The heat capacity of GeTe was measured in the temperature range 220–460 K in two runs. The data are graphically represented in Fig. 2. A linear least-squares analysis of the data yielded the expression

$$C_p = 45.9 + 2.22 \times 10^{-2}\, T\ (\text{J K}^{-1}\ \text{mole}^{-1}) \tag{3}$$

which predicts the heat capacity of GeTe within ± 1.6% in the temperature range 220–460 K. The standard deviation of the data is ± 0.5 J K^{-1} mole^{-1}. The graphical representation of the equation is included in Fig. 2 as a linear plot through the GeTe heat capacity data.

DISCUSSION

The calculation of Debye temperatures

At the Debye temperature C_v has reached about 95% of its limiting value. For

TABLE I

THE DEBYE TEMPERATURE OF GeS, GeSe AND GeTe CALCULATED FROM TABULATIONS OF $D(\theta_D/T)$ AS A FUNCTION OF θ_D/T

T (K)	C_p (J K^{-1} mole^{-1})	C_v (J K^{-1} mole^{-1})	$C_v/6R$ $D(\theta_D/T)$	θ_D/T	θ_D (K)
GeS					
220	45.61	43.09	0.8638	1.7381	382
230	46.11	43.42	0.8704	1.6911	389
240	46.57	43.71	0.8762	1.6486	396
250	46.99	43.95	0.8810	1.6135	403
GeSe					
220	48.47	45.65	0.9151	1.3442	296
230	48.89	45.89	0.9199	1.3038	300
240	49.27	46.09	0.9239	1.2683	304
250	49.62	46.26	0.9273	1.2379	309
GeTe					
220	50.82	47.89	0.9600	0.9072	200
230	51.04	47.95	0.9612	0.8931	205
240	51.26	48.01	0.9624	0.8782	211
250	51.48	48.07	0.9636	0.8654	216

The last figure in the heat capacity values has only calculational significance.

binary compounds with 2 atoms per molecule, the limiting value of C_v is $6R \simeq 50$ J K^{-1} mole^{-1}.

Using the least-square expressions for GeS, GeSe and GeTe, (eqns. 1–3), C_p values were calculated at 220, 230, 240, and 250 K for the three compounds. The values of C_v for GeS, GeSe and GeTe were estimated from the C_p values using the Nernst and Lindemann[9] approximation

$$C_p - C_v = A_0 C_p^2 T/T_m \tag{4}$$

where T_m is the melting point of the solid and A_0 is a universal constant equal to 5.12×10^{-3} J K^{-1} mole^{-1}. The melting points of 931 K[10], 948 K[11], and 996 K[12] have been reported for GeS, GeSe and GeTe, respectively. The results of these calculations are shown in Table I. It is evident from Table I that the C_v values for GeTe at temperatures between 220 and 250 K are greater than 47 J K^{-1} mole^{-1} ($6R \times 0.95$) as compared to the C_v values for GeS and GeSe which are less than 47 J K^{-1} mole^{-1}. These results indicate that the Debye temperature, θ_D, for GeTe is below 220 K, whereas the θ_D values for GeS and GeSe are greater than 250 K.

To compute θ_D for GeS, GeSe and GeTe, the ratio $C_v/6R$ was calculated for each compound at 220 to 250 K. The dimensionless ratio $C_v/6R$ is equal to $D(\theta_D/T)$, the Debye function for binary compounds

$$C_v = 6R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D} \frac{e^x x^4}{(e^x - 1)^2}\, dx = 6R\, D(\theta_D/T) \tag{5}$$

$[x = h\nu/kT]$

Using a tabulation of the Debye function[13], values of θ_D were calculated at the four temperatures.

Generally, heat capacity determinations at lower temperatures are more reliable for the calculation of θ_D because C_v has a greater temperature dependence at lower temperatures and effects of anharmonicity are smaller. With this fact in mind, the trends in the θ_D values for GeS, GeSe and GeTe as a function of temperature suggest that estimated θ_D values are about 360, 280 and 180 K for GeS, GeSe and GeTe, respectively. The θ_D value of 180 K for GeTe can be compared to a reported value of 166 K based on low temperature heat capacity measurements[14] in the range 0.1–1.1 K. The Debye temperature for GeTe is the lowest of the three compounds studied in this work and must be the least accurate from our relatively high temperature measurements. In view of this, the agreement with the result obtained at the lower temperature[14] is gratifying. It furthermore indicates that no low temperature complications seem to exist in the heat capacities.

TABLE 2

THE DEBYE TEMPERATURE, DEBYE FREQUENCY, REDUCED MASS AND AVERAGE FORCE CONSTANT OF IV–VI COMPOUNDS

Compound (Crystal structure)	*θ_D (K) (Temp. meas.)*[a]	*ν_D ($s^{-1} \times 10^{12}$)*	*μ (kg $\times 10^{-26}$)*	*Average force constant (N/m)*
GeS (orthorhombic)	360 ± 20 (220)	7.50	3.69	81.9
GeSe (orthorhombic)	280 ± 20 (220)	5.83	6.28	84.3
GeTe (rhombohedral)	166 ± 3[14] (1.1)	3.46	7.68	36.3
SnS (orthorhombic)	270[15] (80)	5.63	4.19	52.4
SnSe (orthorhombic)	210[15] (80)	4.35	7.87	59.5
SnTe (cubic)	140[16] (—)	2.92	10.2	34.3
PbS (cubic)	227[17] (200)	4.73	4.61	40.7
PbSe (cubic)	138[17] (200)	2.88	9.49	31.0
PbTe (cubic)	125[17] (200)	2.60	13.1	35.1

[a] ( ) indicates temperature (K) at which θ_D was determined.

The vibration frequency of a solid can be related to an average force constant, B, and the reduced mass, μ, of the vibrating atoms by the equation

$$\nu_D = \frac{1}{2\pi}\sqrt{\frac{B}{\mu}} \tag{6}$$

The reduced mass can be calculated from the expression

$$\mu = \frac{M_m \times M_c}{M_m + M_c} \tag{7}$$

where M_m and M_c are the masses of the metal and chalcogen atoms, respectively. Using the θ_D values for GeS and GeSe determined in these studies and the θ_D value of 166 ± 3 K for GeTe[14], the average force constants for these compounds were calculated. Additionally, literature θ_D values for the tin[15, 16] and lead[17] chalcogenides were used to calculate the average force constants of these compounds. Table 2 lists the Debye temperatures, Debye frequencies, reduced masses and average force constants for the above IV–VI binary compounds. It can be seen from Table 2 that the θ_D values decrease with increasing atomic weight of the chalcogen and of the metal atoms in this series. The average force constants of the metal chalcogenides are apparently a function of crystal structure. For the orthorhombic compounds (GeS, GeSe, SnS, SnSe), the average force constant is higher than for the cubic or rhombohedral structure. The B values for the orthorhombic compounds are nearly twice as large as those for the cubic compounds in this series. The observation that the B values for GeS and GeSe are about equal suggests that the lower θ_D value for GeSe is mainly a result of increased molecular weight and not of binding differences within the respective solids. Similar conclusions may be drawn concerning other IV–VI compounds with similar B values. The rather large difference in the average force constants between the orthorhombic and cubic IV–VI compounds is probably due to the complex nature of the orthorhombic structure as compared to the highly symmetrical NaCl-type structure.

The calculation of absolute entropies from heat capacity data

The Debye function may be used to predict the absolute entropy of a compound according to the equation

$$\frac{S^0}{3R} = \frac{4}{3} D\left(\frac{\theta_D}{T}\right) - \ln\left(1 - e^{-\theta_D/T}\right) \tag{8}$$

We used eqn. (8) to calculate the absolute entropy of the germanium chalcogenides at 220 K and the heat capacity functions as measured in these studies to obtain the absolute entropy S^0_{298} for the compounds.

From tabulations[13] of eqn. (8) and the θ_D values of GeS and GeSe, the absolute entropy at 220 K is 45.2 and 56.5 J K^{-1} mole^{-1} for GeS and GeSe, respectively. Integrating the heat capacity functions of GeS and GeSe from 220 to 298 K yields additional entropy changes of 14.2 and 15.1 J K^{-1} mole^{-1}, respectively. The absolute entropies S^0_{298} for GeS and GeSe are thus 59.4 ± 4.0 and 71.6 ± 4.0 J K^{-1} mole^{-1} respectively. The error limits of ± 4.0 J K^{-1} mole are estimated from the 20 K uncertainty in the θ_D values used to calculate the entropy at 220 K.

The calculation of S^0_{298} for GeTe is based on a somewhat different procedure. Using the θ_D value of 166 ± 3 K [14] the absolute entropy is calculated at 166 K. It is assumed that our GeTe heat capacity function [eqn. (3)] is valid from 166–298 K although the heat capacity was actually measured from 220–460 K. At 166 K the absolute entropy of GeTe is 67.8 J K^{-1} mole and integrating the measured heat capacity adds an additional entropy change of 29.7 J K^{-1} mole^{-1} from 166 to 298 K to yield S^0_{298} = 97.5 ± 4.0 J K^{-1} mole^{-1} for GeTe. A similar calculation based on the θ_D value of 180 ± 20 K for GeTe yields S^0_{298} = 93.7 ± 4.0 J K^{-1} mole^{-1} which is within error limits of the absolute entropy value obtained using the θ_D value of 166 K.

SUMMARY AND CONCLUSIONS

As a result of heat capacity measurements on GeS GeSe and GeTe in the temperature range 220–610 K, θ_D values and average force constants, B, were calculated for these materials and compared to other IV–VI compounds. It is observed that the magnitude of the B values depends upon the crystal structure.

The absolute entropies at 298 K were calculated to be 59.4 ± 4.0, 71.6 ± 4.0 and 97.5 ± 4.0 J K^{-1} mole^{-1} for GeS, GeSe and GeTe, respectively. These values are in close agreement with absolute entropies calculated independently from Knudsen-type vaporization studies, namely, 58.6 ± 6, 70.8 ± 8 and 94.6 ± 8 J K^{-1} mole^{-1} for GeS[18], GeSe[19] and GeTe[20], respectively.

A thermal effect at 520 K observed in the heat capacity measurements of GeS corresponds to a halt in the thermal expansion of the a- and b-axes observed in high temperature X-ray diffraction studies[7] of this compound.

ACKNOWLEDGEMENTS

The authors are pleased to acknowledge the support of this work in part by the National Science Foundation and by the National Aeronautics and Space Administration.

REFERENCES

1 H. Wiedemeier, E. A. Irene and A. K. Chaudhuri, *J. Cryst. Growth*, 13/14 (1972) 393.
2 H. Wiedemeier and E. A. Irene, *Z. Anorg. Allg. Chem.*, 400 (1973) 59.
3 H. Wiedemeier and P. A. Siemers, to be published.
4 U. Gaur, A. Mehta and B. Wunderlich, *J. Therm. Anal.*, 13 (1978) 71.
5 D. C. Ginnings and G. T. Furukawa, *J. Am. Chem. Soc.*, 75 (1953) 522.
6 H. Wiedemeier and A. G. Sigai, *J. Cryst. Growth*, 6 (1969) 67.
7 H. Wiedemeier and P. A. Siemers, *Z. Anorg. Allg. Chem.*, 411 (1975) 90.
8 H. Wiedemeier and P. A. Siemers, *Z. Anorg. Allg. Chem.*, 431 (1977) 299.

9 W. Nernst and F. A. Lindemann, *Z. Elektrochem.*, 17 (1911) 817.

10 W. Viaene and G. Moh, *Neues Jahrb. Mineral., Monatsh.*, 6 (1970) 283.

11 L. Ross and M. Bourgon, *Can. J. Chem.*, 47 (1969) 2555.

12 J. P. McHugh and W. A. Tiller, *Trans. AIME*, 218 (1960) 186.

13 G. T. Furukawa and T. B. Douglas, in D. E. Gray (Ed.), *American Institute of Physics Handbook*, McGraw-Hill, New York, 1957, pp. 4–112.

14 L. Finegold, *Phys. Rev. Lett.*, 13 No. 7 (1964) 233.

15 P. V. Gultyaev and A. V. Petrov, *Sov. Phys. Solid State*, 1 (1959) 330.

16 D. H. Damon, C. R. Martin and R. C. Miller, *J. Appl. Phys.*, 34 (1963) 3083.

17 P. Aigrain and M. Balkanski, *Selected Constants Relative to Semiconductors*, Pergamon Press, London, 1961.

18 H. Wiedemeier and P. A. Siemers, to be published.

19 H. Wiedemeier and E. A. Irene, *Z. Anorg. Allg. Chem.*, 404 (1974) 299.

20 H. Wiedemeier and F. C. Klaessig, work in progress.