

Estimation of the Heat Capacity of Some Semiconductor Compounds Using n -Dimensional Debye Functions

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Abstract In the present study, a simple and efficient expression for the accurate and quick calculation of the specific heat capacity of semiconductor compounds is presented on the basis of n -dimensional Debye functions using binomial coefficients. As will be seen, the present formulation yields compact, closed-form expressions which enable the straightforward calculation of the heat capacity of solids for arbitrary temperature values. As an example of the application, the calculation is performed for the specific heat capacity of semiconductor compounds. The calculated results have been compared with those reported in the literature and are found to be in good agreement with those of other studies.

Keywords Binomial coefficient · Debye function · Semiconductor compounds · Specific heat capacity

1 Introduction

The determination of the specific heat capacity of crystals is one of the important topics of condensed matter physics. The specific heat capacity not only represents all modes of thermal motion but it is also a prerequisite for many applications [1–5]. It is well known that a number of binary compounds formed between elements of Groups IV and VI are beneficial semiconducting and photoconducting materials used in optoelectronic devices, electronic rectifiers, and holographic recording systems

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[6–15]. For their importance in technology, it can be useful to know the thermodynamic properties of these semiconductor compounds, such as the heat capacity, entropy, etc.

In this manner, various experimental [16–21] and theoretical [1,2,22–25] techniques have been developed to estimate the specific heat capacities of IV–VI semiconductor compounds, and the different experimental techniques were also used in the low-, medium-, and high-temperature regions.

The heat capacities of the compounds of interest were measured by Wiedemeier et al. [16–18] in the temperature range from 230 K to 580 K using a computer interfaced differential scanning calorimeter. Gul'tyaev and Petrov [19] determined the heat capacity of SnSe at 80 K, also using adiabatic measurements. Bevolo et al. [20] measured the heat capacity of GeTe, SnTe, and PbTe compounds by the heat-pulse method from 0.9 K to 60 K. Aliev et al. [21] determined the low-temperature heat capacity of SnSe in the range from 55 K to 350 K by adiabatic calorimetry. The Einstein model for calculating the heat capacity of semiconductor compounds was used by Ghatak et al. [22]. Rabe and Joannopoulos [23] calculated the heat capacity of SnTe and PbTe using *ab initio* calculations. The thermodynamic functions of SnSe were calculated by Pashinkin et al. [24] in the range from 298.15 K to 700 K.

For the theoretical methods used in the heat capacity calculations, various problems have appeared: (1) the calculations have been made separately in both low- and high-temperature regimes, and (2) some models used in thermophysical property calculations are very time-consuming. Hence, analytical formulas based on well known models, such as the Debye model, have proved to be extremely simple and efficient for calculating the thermodynamic properties of the compounds of interest and to remove the above-mentioned problems [21,25–38].

In the present study, a simple and efficient analytical expression to calculate the heat capacity of IV–VI semiconductor compounds over a wide temperature range is presented using an n -dimensional Debye function involving binomial coefficients [39]. The validity and reliability of the obtained analytical expression is tested by applying it to the specific heat capacity of some IV–VI semiconductor compounds, GeS, GeSe, GeTe, and SnSe.

2 Expression for Specific Heat Capacity and Its Application to Semiconductor Crystals

The isochoric heat capacity in the Debye approximation is defined as [2,16–18,31]

$$C_V(T) = 3n_A R B_3(1, x_D) \quad (1)$$

where

$$B_3(1, x_D) = 4D_3(1, x_D) - \frac{3x_D}{e^x - 1} \quad (2)$$

R is the gas constant, $x_D = \theta_D/T$, θ_D is the Debye temperature, n_A is the number of atoms in a molecule of the material (i.e., $n_A = 1$ or 2 for elemental and binary

compounds), and $D_n(s, x_D)$ is the generalized n -dimensional Debye functions, which is given as [40,41]

$$D_n(s, x_D) = \frac{n}{x_D^n} \int_0^{x_D} \frac{x^n}{(e^x - 1)^s} dx. \quad (3)$$

Also, to convert C_V to C_p , and vice versa, one may use the Nernst and Lindemann approximation [5,16,17],

$$C_p(T) - C_V(T) = A_0 [C_p(T)]^2 \frac{T}{T_m} \quad (4)$$

where $A_0 = 5.1 \times 10^{-3} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and T_m is the melting temperature. Solving Eq. 4 in the usual way, one gets first of all,

$$C_p(T) = \frac{T_m}{2A_0 T} \left[1 - \sqrt{1 - 4A_0 \frac{T}{T_m} C_V(T)} \right] \quad (5)$$

Because of the relatively small magnitude of A_0 , the square root in Eq. 5 can be expanded conveniently into a Taylor series expansion [33]:

$$C_p(T) = C_V(T) + A_0 [C_V(T)]^2 \frac{T}{T_m}. \quad (6)$$

In the above equations, Debye functions symbolize mathematical elements of the theory of the heat capacity of n -dimensional crystals. It can be seen from Eqs. 1 and 5 that the choice of reliable formulas for the evaluation of n -dimensional Debye functions, which are widely used in the equations of physical and chemical sciences, is of prime importance in the accurate and quick calculation of C_V and C_p heat capacities [42,43].

So far, Kaufman and Lipkin [40] have worked out the detailed derivation of Eq. 3. Hardy and coworkers [41] presented a simple method for evaluating the Debye integral in Eq. 3. In addition, Dubinov and Dubinova [30] obtained the exact explicit integral-free expressions for the integral Debye functions and an integral-free expression for the heat capacity of n -dimensional crystals.

Recently, a new formula has been suggested for the calculation of n -dimensional Debye functions using the binomial expansion theorem (for details, see [33,39]) in the following form [31]:

$$D_n(s, x_D) = \frac{n}{x_D^n} \lim_{L \rightarrow \infty} \sum_{m=0}^L (-1)^m F_m(-s) H_{nm}(s, x_D) \quad (7)$$

where

$$H_{nm}(s, x_D) = \frac{n!}{(m+s)!} \left[1 - e^{-x_D(m+s)} \sum_{K=0}^n \frac{x_D^K (m+s)^K}{K!} \right], \quad (8)$$

n and s are integers, and $F_m(n) = n!/[m!(n-m)!]$ is the binomial coefficient. The detailed derivation of the above mentioned formulae can be found in a previous report by the current authors [31].

3 Results and Discussion

We first used the *Mathematica* software system (Version 5.0) to calculate the Debye function using the formula presented in this study. The calculated and compiled values [16–18] of the specific heat capacity for IV–VI semiconductor compounds are shown in Tables 1, 2, 3, and 4.

The calculated heat capacity of the SnSe semiconductor compound in comparison with the data available in the literature is shown in Table 1. It is evident from Table 1 that the results obtained are in excellent agreement with the results of Wiedemeier et al. [16] over the complete temperature range. The largest discrepancy (0.23 %) compared to the compiled values occurred at a temperature of 240 K.

The temperature variation of heat capacities of GeS, GeSe, and GeTe compounds in the temperature range from 220 K to 250 K are shown in Tables 2, 3, and 4. The values obtained from Ref. [17] are also included in Tables 2, 3, and 4. Tables 2 and 3 demonstrate excellent agreement between our results and those of Wiedemeier et al. [17] for binary compounds (GeSe and GeTe). In Table 4, contrary to the

Table 1 Heat capacities C_p of SnSe

T (K)	L	Calculated C_p ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	C_p [16] ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
20	500	2.880	2.88
60	500	27.853	27.85
80	500	35.586	35.53
100	500	40.333	40.35
120	500	43.385	43.42
140	500	45.463	45.52
160	500	46.959	47.04
180	500	48.090	48.03
200	500	48.981	49.13
220	500	49.709	49.65
240	500	50.323	50.46
260	500	50.856	50.95
280	500	51.327	51.38
298.15	500	51.716	51.76
300	500	51.753	51.78
340	500	52.508	52.51
380	500	53.174	53.16
420	500	53.783	53.78
460	500	54.353	54.36
500	500	54.896	54.93

Debye temperature and melting temperature are taken from Ref. [16] ($\theta_D = 220$ K, $T_m = 1134$ K)

Table 2 Heat capacities C_p of GeSe

	T (K)	L	Calculated C_p ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	C_p [17] ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
Debye temperature and melting temperature are taken from Ref. [17] ($\theta_D = 280$ K, $T_m = 948$ K)	220	500	48.581	48.47
	230	500	49.038	48.89
	240	500	49.460	49.27
	250	500	49.850	49.62

Table 3 Heat capacities C_p of GeTe

	T (K)	L	Calculated C_p ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	C_p [17] ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
Debye temperature and melting temperature are taken from Ref. [17] ($\theta_D = 180$ K, $T_m = 996$ K)	220	500	50.879	50.82
	230	500	51.149	51.04
	240	500	51.403	51.26
	250	500	51.643	51.48

Table 4 Heat capacities C_p of GeS

	T (K)	L	Calculated C_p ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	C_p [17] ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
Debye temperature and melting temperature are taken from Ref. [17] ($\theta_D = 360$ K, $T_m = 931$ K)	220	500	46.109	45.61
	230	500	46.742	46.11
	240	500	47.322	46.57
	250	500	47.857	46.99

Table 5 Values of Debye functions $D_n(s, x_D)$ for $L = 600$

n	s	x	Eq. 7	Eq. 5 in Ref. [30]
5	1	5	7.686 342 544 180 143 391 528 1×10^{-2}	7.686 342 544 180 192 161 394 4×10^{-2}
8	1	8.5	5.668 715 555 982 402 786 462 7×10^{-3}	5.668 715 555 982 402 786 462 8×10^{-3}
18	1	45	2.012 738 219 420 947 204 807 3×10^{-13}	2.012 738 219 420 947 204 807 3×10^{-13}
12	1	14.6	4.277 349 195 071 272 474 095 8×10^{-5}	4.277 349 195 071 272 474 095 8×10^{-5}
23	1	23.4	9.154 916 225 212 305 920 320 4×10^{-9}	9.154 916 225 212 305 920 320 4×10^{-9}
28	1	31.4	7.178 494 203 747 750 635 687 3×10^{-12}	7.178 494 203 747 750 635 687 3×10^{-12}
32	1	4.5	5.657 349 014 859 927 394 460 2×10^{-2}	5.657 349 014 859 927 394 460 2×10^{-2}

GeSe and GeTe compounds, the values obtained for the GeS compound are very close to the results reported by Wiedemeier et al. [17]. For example, the calculated and compiled values of the specific heat capacity are, respectively, $46.109 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $45.61 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ [17] at 220 K and $46.742 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $46.11 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ [17] at 230 K, and the largest discrepancy is 1.84 % at 250 K. This clearly demonstrates that the formulae obtained yield significant accuracy for arbitrary values of n , s , and x_D .

Examples of computer calculations of the Debye function are shown in Table 5. As can be seen from Table 5, the accuracy of computer calculations obtained in the present algorithm is satisfactory. We see from Table 5 that Eq. 7 displays the most rapid convergence to the numerical result with 17-digit precision when the 340 terms in the infinite summation are taken into account.

4 Conclusion

In conclusion, we have presented a simple analytical expression for calculation of specific heat capacities of semiconductor compounds depending on Debye functions using a binomial coefficient with all integer values of parameters n , s , and x_D . The analytical expression obtained in this work can be used in the study of many physical problems, especially in the calculation of the specific heat capacity. The use of the simple analytical expression for modeling and simulation can be useful in the development of high-quality devices and has wide fields of application. Moreover, using the expression obtained in this study, numerous problems related to the n -dimensional Debye functions can be solved quickly, efficiently, and accurately.

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