*ORIGINAL PAPER*

# AN ANALYTICAL TECHNIQUE FOR EVALUATING HEAT CAPACITY OF GeS, GeSe, GeTe AND SnS SEMICONDUCTORS USING EINSTEIN-DEBYE APPROXIMATION

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*Manuscript received: 06.07.2021; Accepted paper: 15.09.2021;*
*Published online: 30.09.2021.*

***Abstract.*** *A new analytical method for the evaluation of heat capacities of semiconductors (GeS, GeSe, GeTe, and SnS) has been proposed using the Einstein-Debye approximation. These formulae differ from the Debye model representations and they involve a combination of the Einstein and Debye approximations. The proposed method allows developing an increasing accuracy for the determination of the temperature dependent heat capacities of semiconductors GeS, GeSe, GeTe and SnS. The approach suggested in this study for calculation of heat capacities is very well suitable to determine other thermodynamical properties of materials. The temperature dependence of heat capacities of GeS, GeSe, GeTe and SnS semiconductors has been evaluated and shows a good agreement with literature at different temperature ranges.*

***Keywords:*** *specific heat capacities; Einstein-Debye approximation; Debye model; semiconductors.*

## 1. INTRODUCTION

The narrow-band-gap IV-VI semiconductors play important roles in scientific and industrial applications, including in field-effect transistors, photovoltaic devices and photodetectors [1-6]. Since these materials generally have band gaps in the narrow range of 0.5-1.5 eV, this property makes them effective absorbers for incoming solar radiation [7, 8]. Also, it is shown that IV-VI semiconductors have multiple exciton constitutions, which can lead to an increase in the efficiency of solar cells. Note that among various materials, the layered semiconductors SnS, SnSe, GeS and GeSe have attracted intense attention due to their high chemical and environmental stability for photovoltaic cells [9-14]. By considering the industrial applications of semiconductors, it is shown that new various accurate analytical methods should be developed in the study of thermal properties. A large number of scientific articles have been written for the evaluation of the thermal properties of semiconductors, including several experimental and theoretical approaches [15-24]. In literature, most of the studies suggest that calculations of thermodynamics properties have been investigated by using the standard Debye approximation or semi empirical formulae in restricted temperature ranges [15-20]. The experimental method was proposed for calculating heat capacities and absolute entropies of semiconductors, it also provides obtaining the temperature dependent expressions which are derived from the graph quantities, calculated in the paper [16]. In the study [9], the temperature dependent thermoelectric properties of single-crystal GeSe have been investigated. One alternative synthesis approach was suggested for GeS and GeSe

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crystals, also their electrical and optical properties were reported in work [1]. In the article [18], the heat capacity of crystals (GeTe, SeSe, SnTe, PbS, PbSe, and PbTe) and (GeS, GeSe, SnS, $GeS_2$, and $SnS_2$) have been evaluated in the low temperature range by the Debye method which is only convenient for the acoustic branches. Also by using the Debye model, the calculation results have been presented for the heat capacities of (GeS, GeSe, GeTe,and SnS) crystals [19] and other materials [17].

Thus, taking into account the analytical Einstein-Debye suggested method [25, 26], this paper aims to propose an accurate formulation for the evaluation of the heat capacities of semiconductors in the arbitrary temperature range. In recent studies [27-31], successful results were obtained for the calculation of the heat capacities of materials using the Einstein-Debye approach. The new approximation obtained here provides an effective way to calculate high and low temperature behavior of the heat capacities of semiconductors.

## 2. BASIC FORMULAS AND EINSTEIN-DEBYE APPROXIMATION

Explicit semi-empirical expressions can also be found for heat capacities of semiconductors in studies [15, 16, 37] as following forms:

1. for $GeS$, in the temperature range $220 \le T \le 610\,K$

$$C_P = 46.5 + 1.49\times10^{-2}\,T - 2.01\times10^{5}\,T^{-2}\,(JK^{-1}mol^{-1}) \tag{1}$$

2. for $GeSe$ in the temperature range $220 \le T \le 610\,K$

$$C_P = 50.2 + 9.60\times10^{-3}\,T - 1.87\times10^{5}\,T^{-2}\,(JK^{-1}mol^{-1}) \tag{2}$$

3. for $GeTe$ in the temperature range $220 \le T \le 460\,K$

$$C_P = 45.9 + 2.22\times10^{-3}\,T\,(JK^{-1}mol^{-1}) \tag{3}$$

4. for $SnS$ in the temperature range $100 \le T \le 870\,K$

$$C_P = Exp(0.114905(\ln T)^3 - 1.99273(\ln T)^2 + 11.6659\ln T - 19.144)(JK^{-1}mol^{-1})\,. \tag{4}$$

To obtain the specific heat capacity at constant pressure and volume, we use the formulas presented in Refs. [31, 32], respectively:

$$C_P(T) = C_V(T)\left(1 + \frac{A_0 T}{T_m} C_V(T)\right), \tag{5}$$

$$C_V(T) = 3N_A k_B M\left(T, \theta_D, \theta_E\right)\ , \tag{6}$$

where $A_0 = 5.1x10^{-3}\,J^{-1}K\,mol$ , $T$ is the absolute temperature, $T_m$ is the melting temperature, $N_A$ is the Avogadro number, $k_B$ is the Boltzmann constant, $\theta_D$ is the Debye temperature and $\theta_E$ is the Einstein temperature. By using the Debye-Einstein approximation for the $M(T, \theta_D, \theta_E)$ function, we get an entirely efficient formula as [25, 26]:

$$M\left(T, \theta_D, \theta_E\right) = L_V\left(T, \theta_D\right) + (s-1)A\left(T, \theta_E\right), \tag{7}$$

where $s$ is the number of atoms in one lattice point and the function $L_V(T,\theta_D)$ is determined as:

$$L_V(T,\theta_D) = (n+1)D_n\left(1,\frac{\theta_D}{T}\right) - \frac{\theta_D}{T}\frac{n}{e^{\frac{\theta_D}{T}}-1}. \tag{8}$$

Here, the quantity $n$ takes the value 3-5 for alloys and metals. The functions $D_n(\beta,x)$ appearing in Eq. (8) are the *n*-dimensional Debye functions [33]:

$$D_n(\beta,\mathrm{x}) = \frac{n}{x^n}\int_0^x \frac{t^n}{(e^t-1)^\beta}dt\,. \tag{9}$$

where $\beta$ takes an integer and non-integer values and $\beta=1$ corresponds to the Einstein-Debye approximation. The function $A(T,\theta_E)$ in Eq. (3) is the Einstein function and determined by the following formula:

$$A(T,\theta_E) = \left[\frac{\theta_E}{2T}\frac{1}{\sinh\left(\frac{\theta_E}{2T}\right)}\right]^2. \tag{10}$$

As seen from Eq.(7), one of the fundamental problems is an accurate evaluation of *n*-dimensional Debye functions. Recently, the general analytical relation for *n*-dimensional Debye functions $D_n(\beta,x)$ is presented in the work [34] as:

$$D_n(\beta,x) = \frac{n}{x^n}\lim_{N\to\infty}\sum_{i=0}^{N}(-1)^i F_i(-\beta)\frac{\gamma(n+1,(i+\beta)x)}{(i+\beta)^{n+1}} \tag{11}$$

where $N$ is the upper limit of series. Here, the functions $F_i(-\beta)$ and $\gamma(\alpha,y)$ are the binomial coefficients and incomplete gamma functions defined as, respectively [35-38]:

$$F_m(n) = \frac{1}{m!}\prod_{i=0}^{m-1}(n-i) \tag{12}$$

and

$$\gamma(\alpha,y) = \int_0^y t^{\alpha-1}e^{-t}dt\,. \tag{13}$$

The most general reproduced formulas have been developed in [39] for the accurate calculation of incomplete gamma functions.

## 3. RESULTS AND DISCUSSION

It should be noted that the problem of the evaluation of theoretical information about heat capacities of semiconductors are given approximately by the literatures presentation of results in the form of small-scale temperature ranges. The new approach may yield the progress of further thermodynamics properties, in particular using a new identity for n dimensional Debye functions.

We present a new approach for the calculation of the heat capacities of semiconductors as a function of temperature using formulas (5) and (7). The all calculations were performed in the Mathematica 7.0 program software. The comparison of obtained results with well known literature data is given in Figs. 1-4. Considering that most of the applications of semi empirical formulae do not have a high deviation from the full analytical methods, we conclude that the approximation is useful in the calculation of the heat capacities as an alternative to its formulation described by Eqs. (1)-(4) for practical applications in the given temperature ranges. We demonstrate an efficient method for the analytical evaluation of heat capacities in a wide range of temperatures. As seen from Figs. 1-4, the evaluation of the heat capacities with the Einstein-Debye approach yields convenient results, also could provide a new attempt to the calculation of other thermal properties of semiconductors. We believe some essential discrepancy with Eqs. (1)-(4) associated with the use of approximate formulas in restricted temperature ranges for calculation of heat capacity. The Einstein-Debye method, one of the well known new developments in theoretical approaches, has provided more accurate results for the evaluation of the thermodynamic quantities of solid materials.

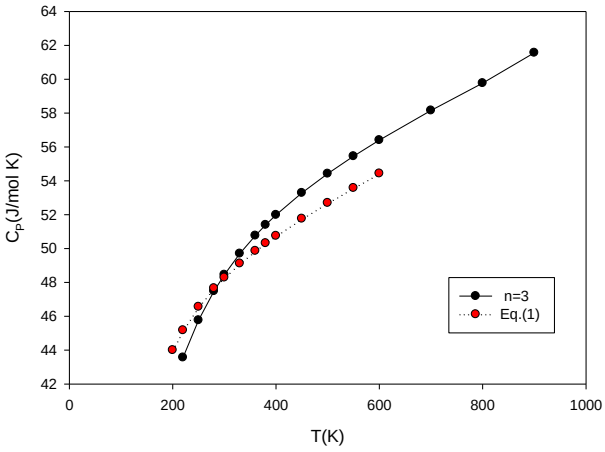


**Figure 1. The temperature dependence of $C_p$ heat capacity at constant pressure for GeS ($T_m$ = 931K, $\theta_D$ = 360K, $\theta_E$ = 379K).**

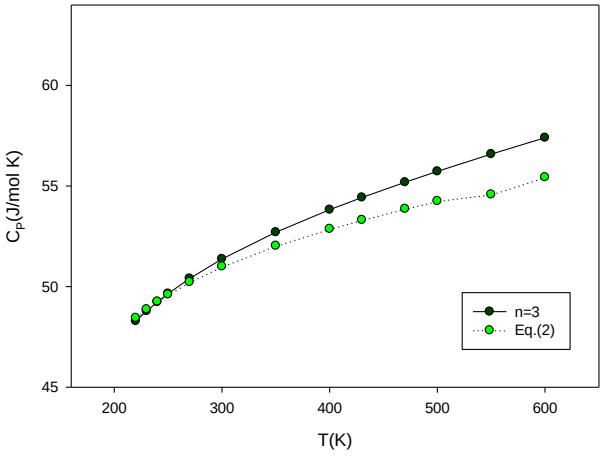


**Figure 2. The temperature dependence of $C_p$ heat capacity at constant pressure for GeSe ($T_m$ = 948K, $\theta_D$ = 280K, $\theta_E$ = 235K).**

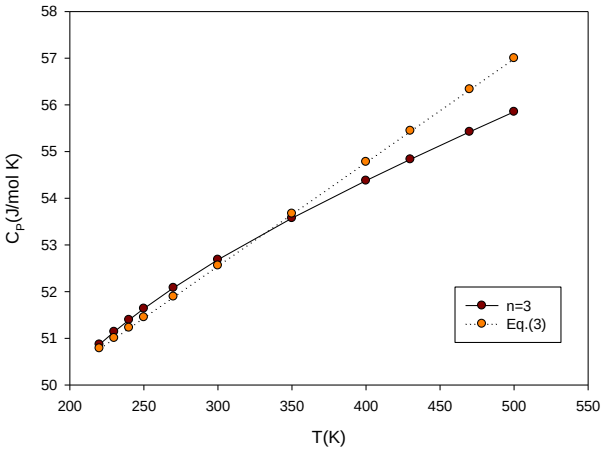


**Figure 3. The temperature dependence of $C_p$ heat capacity at constant pressure for GeTe ($T_m$ = 996K, $\theta_D$ = 180K, $\theta_E$ = 140K).**

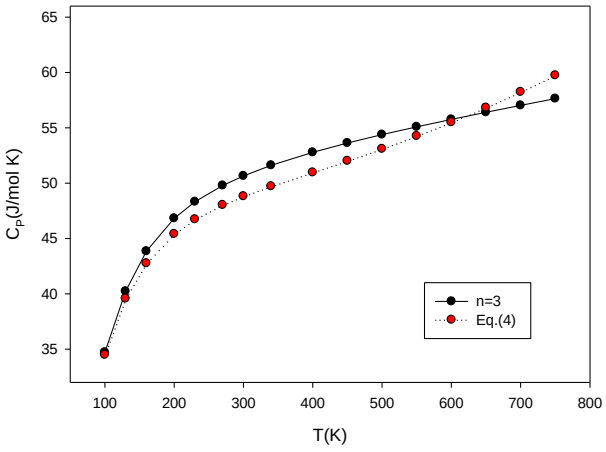


**Figure 4. The temperature dependence of $C_p$ heat capacity at constant pressure for SnS ($T_m$ = 1155K, $\theta_D$ = 270K, $\theta_E$ = 237K) [38].**

## 4. CONCLUSION

In an attempt to find the proposed method for evaluation of the heat capacities have to adequately represent the temperature dependence behavior of more matters. It can be concluded, on the basis of the results obtained, suggested approach allows us to evaluate the heat capacities in the wide range temperature ranges with accuracy and reliability.

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