Heat capacity calculation of the CuAlS₂ semiconductor compound using the Lambert W function

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\textbf{ABSTRACT}

In term of the Lambert W function, simple and reliable analytical expression for the estimation of the specific heat capacity of the CuAlS₂ semiconductor is proposed by using the Lambert Boltzmann distribution. The obtained results have been compared with the corresponding experimental results in the 100-300 K temperature range. The estimated results are in good agreement with the experimental results over the entire temperature range. However, accurate values of the heat capacity cannot be calculated using the standard Boltzmann formula.

1. Introduction

Among with I-III–VI₂ semiconductors compounds, disulphide of copper and aluminum (CuAlS₂) is of special technological interest. It is known that these semiconductor compounds are suitable for many technical applications, such as light emitting devices [1], optical filters [2] and solar cells [3], they are also being studied as materials for Spintronics [4]. The CuAlS₂ semiconductor is also suitable for the use as window material for solar cells and light-emitting diodes since it has a wide direct gap of 3.5 eV.

For optimizing the synthesis of the CuAlS₂ semiconductor compound and estimating its thermodynamic characteristics, the evaluating data on the heat capacities of this semiconductor compound is of great importance. So far, the heat capacity of CuAlS₂ has been measured by the adiabatic calorimeter and were more refining using the least squares method [5]. However, no theoretical methods were used to calculate the heat capacity of CuAlS₂.

The aim of the present study is to present a simple and reliable analytical expression for the estimation of the specific heat capacities of semiconductor compounds such as CuAlS₂ in terms of the Lambert W function using the Lambert Boltzmann distribution in the temperature range 100-300 K.

2. Heat capacities \( C_v \) and \( C_p \) expression and its application to the semiconductor compound CuAlS₂

The expression for internal energy \( U \) and heat capacity \( C_v \) of indistinguishable particles are, respectively,

\[ U_v = 3NkT² \left( \frac{\partial \ln Z}{\partial T} \right)_V \quad \text{and} \quad C_v = \left( \frac{\partial U}{\partial T} \right)_V \]

The constant volume heat capacity is expressed as

\[ C_v = 3NkT² \frac{\partial² \ln Z}{\partial T²} + 6NkT \frac{\partial \ln Z}{\partial T} \] (1)

Here \( k \) is the Boltzmann constant, \( T \) the temperature, \( N \) the Avogadro number and \( Z \) is the partition function. This latter was determined for the Lambert-Boltzmann distribution which is the revised Boltzmann statistics for a finite number of particles established by Kakorin [6].

In the literature to derive the exponential Boltzmann distribution, the Stirling approximation, \( \ln(N!)=N \ln(N)-N \) is used. By applying a more exact version of Stirling’s approximation and using the exact form \( \log N! \), respectively, Kakorin derives two more accurate versions of the Boltzmann distribution for a finite number of particles. The first of these involves the Lambert W function [7]. In particular, the Lambert partition function is [6],

\[ Z_W = -2N_W W(-e^{(-\beta \varepsilon_m -1)}) \] (2)

Here \( N_W \) is the number of particles,

\[ \varepsilon_m(T) = kT \ln \left[ \exp \left( \frac{\Delta \varepsilon}{2kT} \right) - \frac{2N}{e} \left( 1 - \exp \left( \frac{\Delta \varepsilon}{kT} \right) \right) \right] - \frac{\Delta \varepsilon}{2} \]

is the Lambert maximum energy, \( \beta = 1/kT \), \( \Delta \varepsilon = k \theta_E \) where \( \theta_E \), \( k \) are, respectively, the Einstein temperature and the Boltzmann constant and \( W \) denotes
the Lambert $W$ function. This function solves the equation [7].

The Lambert $W$ function allows the explicit solution of entire classes of differential equations, which actually only could be solved numerically and is experiencing today a renaissance in various fields of science and engineering [8–18].

$$W(z) \exp W(z) = z \quad (3)$$

The Lambert $W$ function is a complex function with an infinite number of branches, only two of them having real values. If $x$ is real, then for $-\frac{1}{e} \leq x \leq 0$, there are two possible real values of $W(x)$, as displayed in Figure 1. The branch satisfying $-1 \leq W(x)$ is denoted $W_0(x)$ and the branch satisfying $W(x) \leq -1$ is denoted $W_{-1}(x)$. Also, $W(-1/e) = -1$ and $W(0) = 0$.

Also, the $C_v$ versus $C_p$ relationship can be obtained from the Nernst–Lindemann equation [19,20]

$$C_p(T) - C_V(T) = A_0 \left( C_p(T) \right)^2 \frac{T}{T_m}, \quad (4)$$

Implying that

$$C_p(T) = \frac{T_m}{2A_0T} \left[ 1 - \sqrt{1 - 4A_0 \frac{T}{T_m} C_V(T)} \right], \quad (5)$$

where $A_0 = 5.1 \times 10^{-3}$ J$^{-1}$ K mol and $T_m$ is the melting temperature. The square root in Equation (5) can be expanded conveniently into a Taylor series expansion [21],

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

Inserting Equation (2) into Equation (1) yields

$$C_v(T) = 3N_w kT^2 \left[ \frac{\partial^2 \ln(-2N_w W(-e^{-\beta \varepsilon m - 1}))}{\partial T^2} + 6N_w kT \frac{\partial \ln(-2N_w W(-e^{-\beta \varepsilon m - 1}))}{\partial T} \right] \quad (7)$$

and by replacing $C_v$ in Equation (6), we obtain the expression of the heat capacity $C_p$ as:

$$C_p(T) = \left( 3N_w kT^2 \frac{\partial^2 \ln(-2N_w W(-e^{-\beta \varepsilon m - 1}))}{\partial T^2} + 6N_w kT \frac{\partial \ln(-2N_w W(-e^{-\beta \varepsilon m - 1}))}{\partial T} \right) \frac{T}{T_m} \quad (8)$$

Numerical values of the principal Lambert $W$ function can be computed using packages such as Mathematica and Maple.

3. Results and discussion

Firstly, the method was applied to calculate the values of the specific heat capacity at constant volume $C_v$ which we compared with experimental data [5].

The experimental and our calculated values of heat capacity $C_v$ are presented in Table 1. It is evident from this table that the result obtained is in excellent agreement with the experiment data [5] in the temperature range from 100 to 300 K with a large discrepancy of 0.7% at 120 K, 160 K and 250 K.

In an attempt to confirm the method of calculation proposed in this paper, the specific heat capacity at constant pressure $C_p$ for the semiconductor compound CuAlS$_2$ is calculated in the temperature range 100–300 K. In comparison with the experimental data available in the literature, the calculated result is shown in Table 1. Heat capacities $C_v$ of CuAlS$_2$ with Einstein and melting temperatures are $\theta_E = 306$ K and $T_m = 1495$ K.

Table 1. Heat capacities $C_v$ of CuAlS$_2$ with Einstein and melting temperatures are $\theta_E = 306$ K and $T_m = 1495$ K.

| $T$ (K) | $N_w$ | $C_v$ (J.mol$^{-1}$, K$^{-1}$) | $C_v$ (J.mol$^{-1}$, K$^{-1}$) | Relative error |
|--------|-------|-------------------------------|-------------------------------|----------------|
|        |       | Our calculus                  | Experimental                  |                |
| 100    | 9     | 45.25                         | 45.26                         | 0.0001         |
| 110    | 9     | 49.42                         | 49.51                         | 0.0001         |
| 120    | 9     | 53.30                         | 53.70                         | 0.007          |
| 130    | 9     | 56.84                         | 56.78                         | 0.002          |
| 140    | 9     | 60.21                         | 60.21                         | 0              |
| 150    | 9     | 63.28                         | 63.13                         | 0.002          |
| 160    | 9     | 66.10                         | 65.60                         | 0.007          |
| 170    | 9     | 68.70                         | 68.40                         | 0.004          |
| 180    | 9     | 71.09                         | 70.17                         | 0.001          |
| 190    | 9     | 73.27                         | 73.44                         | 0.002          |
| 200    | 12    | 75.27                         | 75.24                         | 0.0003         |
| 210    | 12    | 77.09                         | 77.22                         | 0.001          |
| 220    | 12    | 78.76                         | 79.56                         | 0.002          |
| 230    | 12    | 80.27                         | 80.07                         | 0.002          |
| 240    | 15    | 81.66                         | 81.33                         | 0.004          |
| 250    | 15    | 82.92                         | 82.33                         | 0.007          |
| 260    | 15    | 84.04                         | 84.11                         | 0.005          |
| 270    | 15    | 85.14                         | 85.12                         | 0.0008         |
| 280    | 15    | 86.13                         | 86.31                         | 0.0009         |
| 290    | 15    | 87.05                         | 87                            | 0.0001         |
| 300    | 15    | 87.92                         | 87.42                         | 0.005          |
Table 2. Heat capacities $C_p$ of CuAlS$_2$ with Einstein and melting

$$\theta_E = 306 \text{ K and } T_m = 1495 \text{ K.}$$

| T (K) | Nw | $C_p$ (J.mol$^{-1}$.K$^{-1}$) | Cp (J.mol$^{-1}$.K$^{-1}$) | Relative error |
|-------|----|-----------------------------|-----------------------------|----------------|
| 100   | 9  | 45.23                       | 45.47                       | 0.005          |
| 110   | 9  | 49.53                       | 49.16                       | 0.007          |
| 120   | 9  | 53.43                       | 53                           | 0.008          |
| 130   | 9  | 57.04                       | 57.38                       | 0.008          |
| 140   | 9  | 60.39                       | 60.10                       | 0.005          |
| 150   | 9  | 63.49                       | 63.22                       | 0.004          |
| 160   | 9  | 66.35                       | 67.01                       | 0.008          |
| 170   | 9  | 68.98                       | 69.34                       | 0.009          |
| 180   | 9  | 71.40                       | 71.33                       | 0.001          |
| 190   | 9  | 73.62                       | 73.04                       | 0.007          |
| 200   | 12 | 75.66                       | 75.33                       | 0.004          |
| 210   | 12 | 77.52                       | 77.89                       | 0.004          |
| 220   | 12 | 79.22                       | 79.07                       | 0.002          |
| 230   | 12 | 80.78                       | 80.99                       | 0.001          |
| 240   | 15 | 82.21                       | 82.71                       | 0.006          |
| 250   | 15 | 83.52                       | 83.56                       | 0.0004         |
| 260   | 15 | 84.72                       | 84.31                       | 0.005          |
| 270   | 15 | 85.83                       | 85.75                       | 0.001          |
| 280   | 15 | 86.86                       | 87.04                       | 0.002          |
| 290   | 15 | 87.83                       | 87.64                       | 0.002          |
| 300   | 15 | 88.75                       | 88.59                       | 0.002          |

Figure 2. The temperature dependence of the heat capacity $C_p$ for CuAlS$_2$ semiconductor compound.

Figure 3. The temperature dependence of the heat capacity $C_v$ for CuAlS$_2$ semiconductor compound.

in Table 2. Our results are in excellent agreement with experimental data obtained by Korzun et al. [5] over the temperature range from 100 to 300 K with the largest discrepancy of 0.9% at 170 K.

For further improvement for this method of calculation, Figures 2 and 3 show respectively the comparison of the value of heat capacity at constant pressure $C_p$ and the heat capacity at constant volume $C_v$ calculated by the standard Boltzmann formula and the Lambert Boltzmann distribution with the experimental data [5]. The Boltzmann formula gives significantly larger discrepancies with the data and a large disagreement appears between both results. This confirms that the standard Boltzmann distribution is unable to accurately represent the specific heat.

4. Conclusion

A new method has been presented to accurately calculate the specific heat capacities of the semiconductor compound CuAlS$_2$ using the Lambert-Boltzmann distribution which is a generalization of the exponential Boltzmann distribution when the number of particles is finite. The calculated results of specific heat capacities relatively to the semiconductor compound CuAlS$_2$ have been compared with those reported in the literature and are found to be in good agreement. By comparison, the standard Boltzmann formula is systematically over-biased.

Disclosure statement

No potential conflict of interest was reported by the author.

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