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New Equations for Lattice and Electronic Heat Capacities, Enthalpies, and Entropies of Solids: Application to Diamond

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New equations for heat capacities, entropies, and enthalpies were applied to the experimental constant volume heat capacity data of diamond. The temperature Θ_V corresponding to $3R/2$ was found to be 468 K. The relationships between dimension, and Θ_V and the Debye temperature were given. Diamond showed the dimensionality crossover from 3 to 2 at after 300 K. Temperature dependences of the Debye temperature and Θ_V were given and non-monotonic behaviors were discussed. The heat capacity and entropy values predicted by the proposed models were compared with the values predicted by the Debye models. The results showed that the proposed models fit the data better than the Debye models. The enthalpy values predicted by the proposed models were compared with the values predicted by the polynomial model and good agreement was obtained.

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1. Introduction

Einstein's single oscillator and Nernst-Lindemann's two oscillator models have used the discrete oscillation frequencies, and these models could not describe well the heat capacities in the low temperature region [1–6]. The Debye model considers that atomic system as a three-dimensional, elastic, isotropic continuum and the heat capacity equation is given by [3–5, 7, 8] :

$$C_V = 9R \left(\frac{T}{\Theta_D(T)} \right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (1)$$

where Θ_D is the Debye temperature, $x = \Theta_D(T)/T$ and R is the gas constant.

The entropy equation in the Debye model is given by [3, 4, 7]:

$$S = 3R \left[\frac{4}{x_D^3} \int_0^{x_D} \frac{x^3 dx}{(e^x - 1)} - \ln(1 - e^{-x_D}) \right] \quad (2)$$

The analytical solutions of integrals in Eqs. (1) and (2) are not known. Therefore, at the intermediate temperatures, the values of heat capacities and entropies must be obtained by numerical integration.

At very low temperatures, where $T \ll \Theta_D$, the following equation is obtained from Eq. (1):

$$C_V \cong \frac{12\pi^4 R}{5} \left(\frac{T}{\Theta_D(T)} \right)^3 \quad (3)$$

Equation (3) is known as the Debye T^3 -law and is assumed to be valid from 0 K up to lattice temperatures of order $\Theta_D(0)/50$, where $\Theta_D(0)$ is the Debye temperature at $T \rightarrow 0$ K. Θ_D depends on temperature. Therefore, it is

often impossible to provide good fittings of Eq. (1) to the given heat capacity data sets with a single Debye temperature over the entire temperature range [4, 9]. These non-Debye behaviors have been given in terms of C_V/T^3 functions [10]. These curves show a non-monotonic behavior in the low temperature region which cannot be explained with the Debye's model.

The equation based on Taylor series expansion has been proposed for the temperature interval $\Theta_D(0)/50 \leq T \leq \Theta_D(0)/10$ [4, 9]. Different models based on the Thirring and exponential series expansions have also been given for the intermediate to high temperature regions, respectively [6]. However, these models are more complex and seven or eight empirical parameters should be determined.

The heat capacity equation at constant volume

$$C_V = 3R \frac{T^n}{T^n + \Theta_V^n(T)}, \quad (4)$$

the heat capacity equation at constant pressure

$$C_P = C_{P_{\max}} \frac{T^n}{T^n + \Theta_P^n(T)}, \quad (5)$$

the electronic heat capacity equation

$$C_{el} = \frac{3}{2} R \frac{T^n}{T^n + T_E^n(T)}, \quad (6)$$

the electronic molar entropy equation

$$S_{el,n} = \frac{3}{2n} R \ln \left(\left(\frac{T}{T_E(T)} \right)^n + 1 \right), \quad (7)$$

the lattice molar entropy equation at constant volume

$$S_{V,n} = \frac{3}{n} R \ln \left(\left(\frac{T}{\Theta_V(T)} \right)^n + 1 \right), \quad (8)$$

the lattice molar entropy equation at constant pressure

$$S_{P,n} = \frac{C_{P_{\max}}}{n} \ln \left(\left(\frac{T}{\Theta_P(T)} \right)^n + 1 \right), \quad (9)$$

the lattice molar enthalpy equations at constant pressure for $n = 1, 2$, and 3 :

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$$H_{p,n=1} = C_{P_{\max}} \left[T + \theta_P \ln \left(\frac{\theta_P}{T + \theta_P} \right) \right], \quad (10)$$

$$H_{p,n=2} = C_{P_{\max}} \left[T - \theta_P \tan^{-1} \left(\frac{T}{\theta_P} \right) \right], \quad (11)$$

$$H_{p,n=3} = C_{P_{\max}} \left[-\frac{\pi}{6\sqrt{3}} \theta_P + T - \frac{\theta_P}{3} \ln(\theta_P + T) + \frac{\theta_P}{6} \ln(\theta_P^2 - \theta_P T + T^2) - \frac{\theta_P}{\sqrt{3}} \tan^{-1} \left(\frac{2T - \theta_P}{\sqrt{3}\theta_P} \right) \right] \quad (12)$$

the lattice molar enthalpy equations at constant volume for $n = 1, 2,$ and 3 :

$$H_{V,n=1} = 3R \left[T + \theta_V \ln \left(\frac{\theta_V}{T + \theta_V} \right) \right], \quad (13)$$

$$H_{V,n=2} = 3R \left[T - \theta_V \tan^{-1} \left(\frac{T}{\theta_V} \right) \right], \quad (14)$$

$$H_{V,n=3} = 3R \left[-\frac{\pi}{6\sqrt{3}} \theta_V + T - \frac{\theta_V}{3} \ln(\theta_V + T) + \frac{\theta_V}{6} \ln(\theta_V^2 - \theta_V T + T^2) - \frac{\theta_V}{\sqrt{3}} \tan^{-1} \left(\frac{2T - \theta_V}{\sqrt{3}\theta_V} \right) \right], \quad (15)$$

the electronic molar enthalpy equations for $n = 1, 2,$ and 3 :

$$H_{el,n=1} = \frac{3}{2}R \left[T + T_E \ln \left(\frac{T_E}{T + T_E} \right) \right], \quad (16)$$

$$H_{el,n=2} = \frac{3}{2}R \left[T - T_E \tan^{-1} \left(\frac{T}{T_E} \right) \right], \quad (17)$$

$$H_{V,n=3} = \frac{3}{2}R \left[-\frac{\pi}{6\sqrt{3}} T_E + T - \frac{T_E}{3} \ln(T_E + T) + \frac{T_E}{6} \ln(T_E^2 - T_E T + T^2) - \frac{T_E}{\sqrt{3}} \tan^{-1} \left(\frac{2T - T_E}{\sqrt{3}T_E} \right) \right], \quad (18)$$

were given in Ref. [11].

Substituting $n = 3$ into Eq. (4) gives the following equation at low temperature:

$$C_V = 3R \left(\frac{T}{\theta_V(T)} \right)^3. \quad (19)$$

From Eq. (3) and Eq. (19), the following equation is obtained:

$$\theta_V(T) = \theta_D(T) \left(\frac{5}{4\pi^4} \right)^{1/3}. \quad (20)$$

In this study, the heat capacity, enthalpy, and entropy equations given above will be applied to the constant volume heat capacity data of diamond and the results will be compared with the Debye and polynomial models.

2. Results and discussion

Experimental heat capacity data at constant volume of diamond for the temperature range from 25 K to 1100 K were obtained from Refs. [12, 13] and are shown in Fig. 1. The value of θ_V was found to be 468 K. The value of $\theta_D(0)$ was given to be about 2230 K in Refs. [4, 8]. The heat capacity values calculated by using $\theta_D = 2230$ K in Eq. (1) and the heat capacity values calculated by using $\theta_V = 468$ K and $n = 3$ and $n = 2$ in Eq. (4) are shown in Fig. 1.

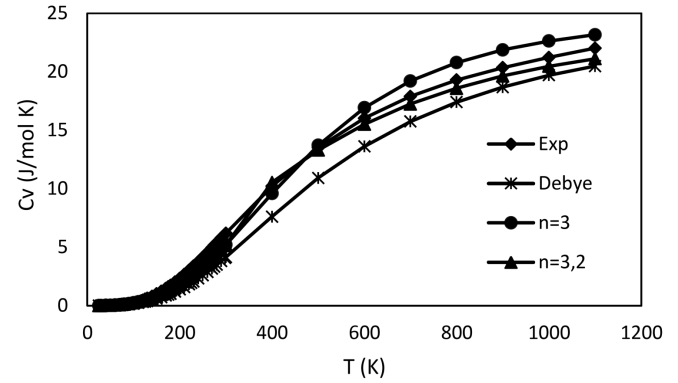


Fig. 1. Temperature dependence of heat capacity C_V of diamond.

The $\theta_D(T)$ values were calculated from the numerical solution of Eq. (1). Temperature dependence of $\theta_D(T)$ of diamond is shown in Fig. 2. The value of $\theta_D(T)$ increases monotonously from 1822 K to the maximum 2242 K with increasing temperature from 25 K to 60 K and then decreases towards 1860 K at about 160 K.

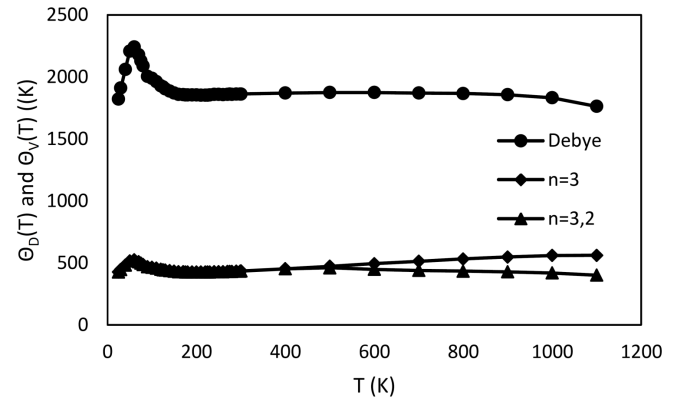


Fig. 2. Temperature dependence of $\theta_D(T)$ and $\theta_V(T)$ of diamond.

The following equation is obtained from Eqs. (4) and (20):

$$n = \frac{\log \left(\frac{3R}{C_V} - 1 \right)}{\log \left(\theta_D(T) \left(\frac{5}{4\pi^4} \right)^{1/3} / T \right)}. \quad (21)$$

The temperature and $\Theta_D(T)$ dependence of n of diamond is shown in Fig. 3. The value of n is about 3 from 25 K to 300 K and exhibits a crossover from 3 to 2 at about 300 K. After 600 K, n takes the value of about 2. Figure 2 and Eq. (21) show that $\Theta_D(T)$ depends on temperature and n .

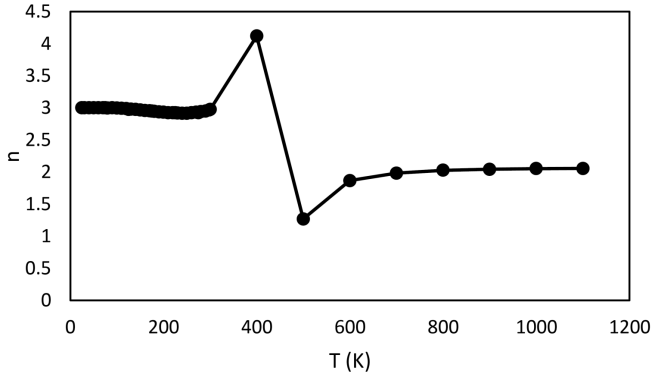


Fig. 3. Temperature dependence of dimension n of diamond.

The following equation is obtained from Eq. (4):

$$\Theta_V(T) = T \left(\frac{3R}{C_V} - 1 \right)^{1/n}. \quad (22)$$

The $\Theta_V(T)$ values were calculated by using $n = 3$ at all temperatures, and by using $n = 3$ from 25 K to 300 K and by using $n = 2$ from 400 K to 1100 K in Eq. (22). Figure 2 shows that the temperature dependence of $\Theta_V(T)$ and $\Theta_D(T)$ is similar.

Figure 4 shows the non-monotonic behavior of the C_V/T^3 function at low temperatures. n was taken to be 3 in this function. It is seen from Eqs. (3) and (19) that the C_V/T^3 is inversely proportional to $\Theta_D^3(T)$ and $\Theta_V^3(T)$. Therefore, the C_V/T^3 function shows the inverse behavior to $\Theta_D^3(T)$ and $\Theta_V^3(T)$.

The root mean square error of prediction (RMSEP) is obtained from the following equation:

$$\text{RMSEP}(C) = \left[\frac{\sum_{i=1}^m (C_{V_{\text{pred}}} - C_{V_{\text{exp}}})^2}{m} \right]^{1/2}, \quad (23)$$

where $C_{V_{\text{exp}}}$ is the experimental heat capacity, $C_{V_{\text{pred}}}$ is the predicted heat capacity and m is the number of heat capacities. The value of RMSEP obtained for the proposed model by using $\Theta_V(T) = 468$ K and $n = 3$ from 25 K to 300 K and $n = 2$ from 400 K to 1100 K was found to be 0.5671. The value of RMSEP obtained for the Debye model by using $\Theta_D(0) = 2230$ K was found to be 1.317. These results show that the proposed model fits the experimental data better than the Debye model at the given conditions.

The values of entropies of diamond obtained from the Debye, proposed and polynomial models are shown in Fig. 5.

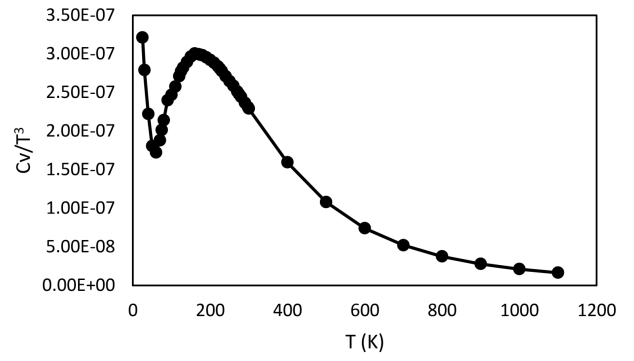


Fig. 4. C_V/T^3 versus T of diamond.

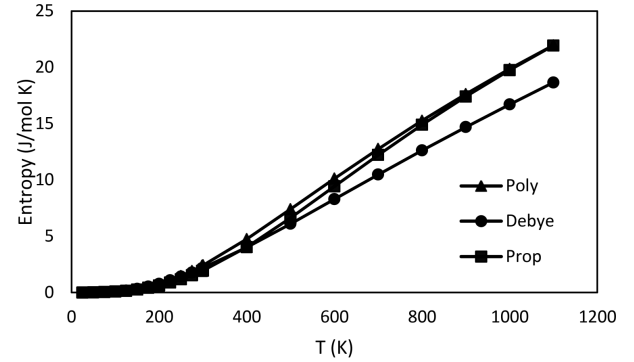


Fig. 5. Temperature dependence of entropy of diamond.

The RMSEP values for entropy are obtained from the following equation:

$$\text{RMSEP}(S) = \left[\frac{\sum_{i=1}^m (S_{\text{pred}} - S_{\text{poly}})^2}{m} \right]^{1/2}, \quad (24)$$

where S_{poly} is the entropy obtained from the polynomial model and S_{pred} is the entropy obtained from proposed and the Debye models. The values of RMSEP obtained for the proposed and the Debye models were found to be 0.3682 and 1.501, respectively. These results and Fig. 5 show that the proposed model fits the data better than the Debye model.

Enthalpy equation cannot be obtained from the Debye model. The enthalpy values of diamond obtained from the proposed and polynomial models are shown in Fig. 6.

The RMSEP value for enthalpy is obtained from the following equation:

$$\text{RMSEP}(H) = \left[\frac{\sum_{i=1}^m (H_{\text{pred}} - H_{\text{poly}})^2}{m} \right]^{1/2}, \quad (25)$$

where H_{poly} is the enthalpy obtained from polynomial model and H_{pred} is the enthalpy obtained from the proposed model. The value of RMSEP was found to be 93.22. This result and Fig. 6 show that good agreement has been obtained between the proposed and polynomial models.

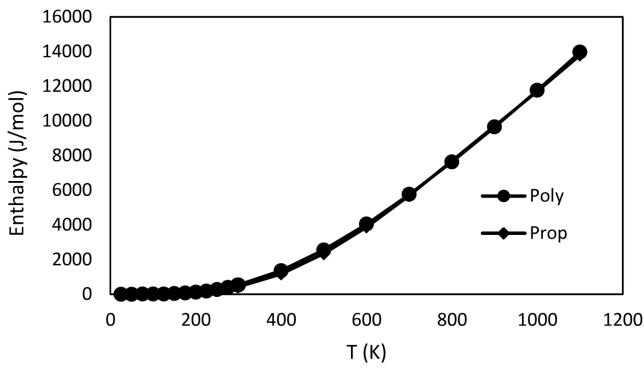


Fig. 6. Temperature dependence of enthalpy of diamond.

3. Conclusion

The value of Θ_V was found to be 468 K for diamond. Diamond shows the dimensionality crossover from $n = 3$ to $n = 2$ after 300 K. The temperature and n dependences of $\Theta_D(T)$ and $\Theta_V(T)$ were given and non-monotonic behavior was discussed. The heat capacity and entropy values obtained by the proposed models were compared with the values obtained by the Debye models by using $\Theta_D(0) = 2230$ K. The results have shown that the proposed models fit the data better than the Debye models at the given conditions. Enthalpy equation cannot be obtained from the Debye model. Good agreement has been found between the enthalpy values obtained by the proposed and the polynomial models.

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