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Thermal energy of ionic solids

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ABSTRACT

In the present paper, we present a method to predict the temperature dependence of thermal energy from room temperature to their melting temperatures at atmospheric pressure i.e., $P = 1$ bar or 10^5 Pa. We find that the calculated results of thermal energy are in good agreement with the experimental data. We employ the present relationship to NaCl and KCl to validate the present model. Present study also reveals that the temperature dependence of thermal energy shows linearity with isothermal bulk modulus. A close agreement between results and experimental data discloses the validity of present work.

1. Introduction

Thermal pressure is having an important role to study the thermodynamic and thermoelastic properties of solids. For understanding the adequacy of pressure–volume–temperature relationships, we need isothermal as well as isobaric equation of state (EoS). Anderson [1] scripted the EoS in terms of thermal pressure as follows:

$$P(V, T) = P(V, T_0) + \Delta P_{th} \tag{1}$$

where $P(V, T_0)$ constitutes the isothermal pressure–volume relationship at $T = T_0$ (initial temperature). ΔP_{th} is the difference in the values of thermal pressures at two temperatures:

$$\Delta P_{th} = P_{th}(T) - P_{th}(T_0) \tag{2}$$

At zero pressure i.e., $P(V, T) = 0$, Eq. (1) becomes

$$-\Delta P_{th} = P(V, T_0) \tag{3}$$

$$-\left(\frac{V}{V_0}\right)\Delta P_{th} = \left(\frac{V}{V_0}\right)P(V, T_0) \tag{4}$$

$$-\left(\frac{V}{V_0}\right)^2\Delta P_{th} = \left(\frac{V}{V_0}\right)^2 P(V, T_0) \tag{5}$$

where V_0 is the volume at $T = T_0$ and $P = 1$ bar or 10^5 Pa. The right hand sides of Eqs. (3)–(5) can be expanded in power of $(V - V_0)$ in Taylor series. We can expand f, a function of volume, as

$$f = f_0 + \left(\frac{df}{dV}\right)_0 (V - V_0) + \frac{1}{2}\left(\frac{d^2f}{dV^2}\right)(V - V_0) + \ldots \tag{6}$$

Using Eqs. (3)–(6), we get

$$\Delta P_{th} = K_0\left(\frac{V}{V_0} - 1\right) - \frac{1}{2}K_0\left(K_0{}' + 1\right)\left(\frac{V}{V_0} - 1\right)^2 \tag{7}$$

$$\Delta P_{th} = \frac{[K_0((V/V_0) - 1) - (1/2)K_0(K_0{}' - 1)((V/V_0) - 1)^2]}{(V/V_0)} \tag{8}$$

$$\Delta P_{th} = \frac{[K_0((V/V_0) - 1) - (1/2)K_0(K_0{}' - 3)((V/V_0) - 1)^2]}{(V/V_0)^2} \tag{9}$$

where K_0 and $K_0{}'$ are respectively isothermal bulk modulus and its first order pressure derivative at room temperature i.e., $T = T_0 = 300$ K and at atmospheric pressure i.e., $P = 1$ bar or 10^5 Pa. Eq. (7) is derived by Shanker et al. [2] by expanding the lattice potential energy in power of $(V - V_0)$ in the form of Taylor series expansion. Eq. (8) has been derived by Singh [3] employing the method of expanding the product of pressure and volume in power series of $(V - V_0)$. Eq. (9) has been formulated by Shanker and Kushwah [4] by expanding the product of PV^2 in power of $(V - V_0)$. In fact, Eqs. (7)–(9) can be obtained from the Taylor series expansion of P, PV and PV^2 in power of change in volume $(V - V_0)$ due to advance in temperature respectively.

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The following relationship represents the link between thermal pressure and thermal energy

$$\Delta P_{th} = \rho\gamma E_{th} \tag{10}$$

where ρ is density and γ is the Gruneisen parameter.

In the present study, we have formulated the simple and straightforward model to find out the temperature dependence of thermal energy for NaCl and KCl from room temperature to their melting temperatures at atmospheric pressure i.e. $P = 1$ bar or 10^5 Pa. The dependence of Anderson–Gruneisen parameter on volume is based on Tallon model [5]. The solids NaCl and KCl are considered for the study because of availability of the experimental data up to a wide range of temperature at atmospheric pressure i.e., $P = 1$ bar or 10^5 Pa for the sake of comparison. The method of analysis is given in Section 2 and the results are discussed in Section 3.

2. Method of analysis

The isothermal Anderson–Gruneisen parameter δ_T is defined [1]

$$\delta_T = -\frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P \tag{11}$$

where α is thermal expansivity and K_T is isothermal bulk modulus. Using the following relation

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{12}$$

in Eq. (11) we get

$$\delta_T = -\frac{V}{K_T}\left(\frac{\partial K_T}{\partial V}\right)_P \tag{13}$$

Following the work of Tallon [5], we consider δ_T to depend on volume as

$$\delta_T = \delta_{T_0}\left(\frac{V}{V_0}\right) \tag{14}$$

Inserting Eq. (14) into Eq. (13) and then integrating the resulting expression under isobaric conditions, we obtain

$$K_T = K_0 \exp\left[-\delta_{T_0}\left\{\left(\frac{V}{V_0}\right) - 1\right\}\right] \tag{15}$$

where K_0, δ_{T_0} are respectively the isothermal bulk modulus (K_T) and Anderson–Gruneisen parameter $\left(\delta_T\right)$ at room temperature $T = T_0 = 300$ K and atmospheric pressure i.e., $P = 1$ bar or 10^5 Pa.

It is known [6] that there exists a linear relationship between isothermal bulk modulus and change in thermal pressure starting from room temperature. Such linear relationship can be written as

$$K_T = K_0 - M\Delta P_{th} \tag{16}$$

where M represents the slop of the plot between isothermal bulk modulus versus change in thermal pressure. Although, Singh [6] has written that such parameter is equivalent to Anderson–Gruneisen parameter remains unchanged with the change in temperature or volume. However, in the present study we use the fact that Anderson–Gruneisen parameter is dependent on volume. So here the parameter M represents the slop of the plot i.e., it is purely an empirical parameter obtained graphically [7]. Combination of Eqs. (16) and (15) results the following expression for thermal pressure

$$\Delta P_{th} = \frac{K_0}{M}\left[1 - \exp.\left\{\delta_{T_0}\left(1 - \left(\frac{V}{V_0}\right)\right)\right\}\right] \tag{17}$$

If we use Eqs. (10) and (17) then we get the expression for computing thermal energy as

$$E_{th} = \frac{K_0[1 - \exp.\{\delta_{T_0}(1 - (V/V_0))\}]}{M\rho\gamma} \tag{18}$$

And the combination of Eqs. (9) and (10) gives the following relation

$$E_{th} = \frac{[K_0((V/V_0) - 1) - (1/2)K_0(K_0{}' - 3)((V/V_0) - 1)^2]}{(V/V_0)^2\rho\gamma} \tag{19}$$

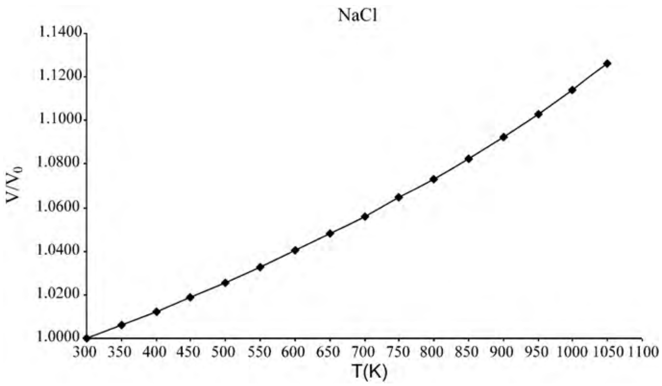

Fig. 1. Plot between V/V_0 [19] versus T (K) for NaCl.

3. Results and discussions

According to well-known Gruneisen relation [8], Gruneisen parameter γ can be written as

$$\gamma = \frac{\alpha K_T V}{C_V} \tag{20}$$

where α, K_T and C_V are respectively the thermal expansivity, isothermal bulk modulus and heat capacity at constant volume. Many researchers [1,9,10] have adopted that C_V remains constant. And αK_T also remains constant [1,9,11–18] at high temperatures i.e., $T\rangle\theta_D$, θ_D is Debye temperature. Thus, Eq. (20) becomes

$$\frac{\gamma}{\gamma_0} = \frac{V}{V_0} \tag{21}$$

or

$$\frac{\gamma}{\gamma_0} = \frac{\rho_0}{\rho} \tag{22}$$

or

$$\gamma\rho = \text{constant} \tag{23}$$

This is true that $\gamma\rho$ is nearly constant, this assumption is consistent with the approximation that the temperature dependence of γ at constant V is nearly zero i.e., $(\partial\gamma/\partial T)_V = 0$ (Mie–Gruneisen approximation), it generally decreases as the volume decreases [1]. Therefore, we prefer to take the assumption that $\gamma\rho$ remains constant at high temperatures $\left(T\rangle\theta_D\right)$, does not hold for low temperatures $\left(T\langle\theta_D\right)$.Combination of Eqs. (18) and (23) we get the following relationship

$$E_{th} = \frac{K(T_0,0)[1 - \exp.\{\delta(T_{0,}0)(1 - (V/V_0))\}]}{M\rho_0\gamma_0} \tag{24}$$

Applying the same sense, Eq. (19) becomes

$$E_{th} = \frac{[K_0((V/V_0) - 1) - (1/2)K_0(K_0{}' - 3)((V/V_0) - 1)^2]}{(V/V_0)^2\rho_0\gamma_0} \tag{25}$$

where ρ_0 and γ_0 are respectively density and Gruneisen parameter at $T = T_0 = 300$ K and at atmospheric pressure i.e., $P = 1$ bar or 10^5 Pa. To investigate the temperature dependence of thermal energy from Eqs. (24) and (25) in which we have taken the values of V/V_0 from ref. [19], we plot the graph between V/V_0 and T(K) in Figs. 1 and 2 for NaCl and KCl respectively (Table 1).

Srivastava and Sharma [20] have found that the thermal pressure evaluated by Eq. (9) is the least deviated from the experiment and shows the superiority of Eq. (9) over other Eqs. (7) and (8). So we use Eq. (9) to evaluate thermal pressure of NaCl and KCl here. We have predicted thermal energy from room temperature to melting temperature by using Eqs. (24) and (25). Since V/V_0 is the function of T and thermal energy is the function of V/V_0. In this way

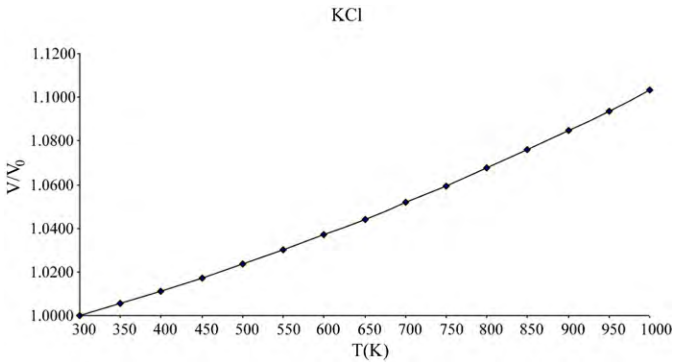

Fig. 2. Plot between V/V_0 [19] versus T (K) for KCl.

Table 1
Input parameters used in calculations.

Parameter	NaCl	KCl
K_0(GPa)	24 [1]	17 [1]
δ_{T_0}	5.56 [1]	5.84 [1]
K_0'	5.38 [1]	5.46 [1]
$\rho_0\left(10^3\ \mathrm{kg/m^3}\right)$	2.159 [1]	1.982 [1]
γ_0	1.59 [1]	1.44 [1]
M	5.9623 [7]	5.9181 [7]

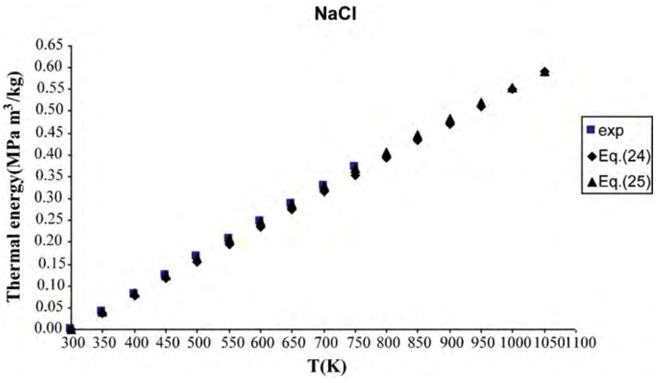

Fig. 3. Comparison of temperature dependence of thermal energy for NaCl in the present study (Eqs. (24) and (25) alongwith experimental data at atmospheric pressure.

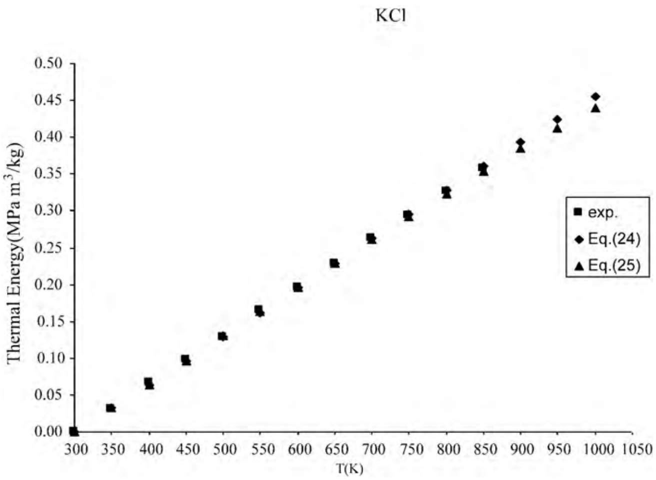

Fig. 4. Comparison of temperature dependence of thermal energy for KCl in the present study (Eqs. (24) and (25) alongwith experimental data at atmospheric pressure.

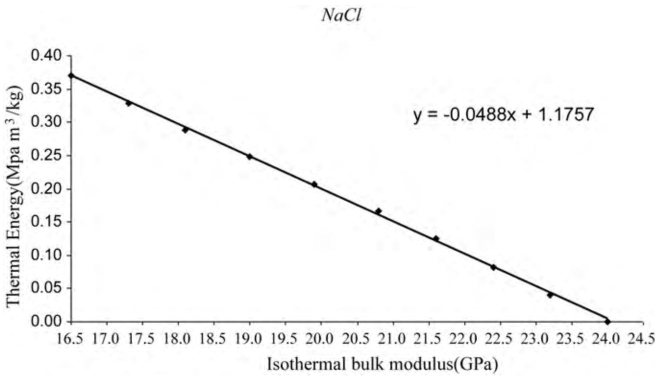

Fig. 5. Plot between thermal energy and isothermal bulk modulus for NaCl from room temperature to 750 K.

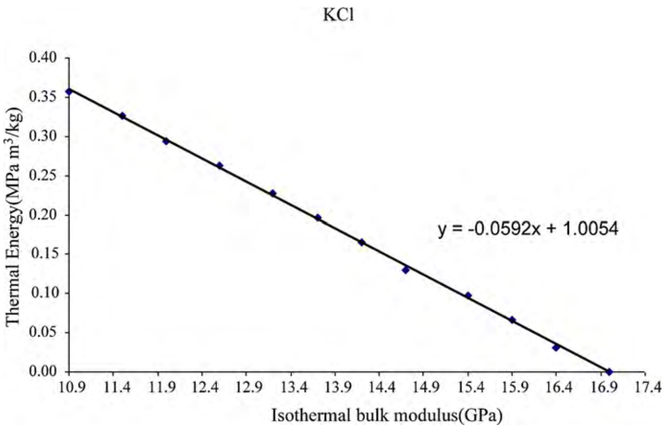

Fig. 6. Plot between thermal energy and isothermal bulk modulus for KCl from room temperature to 850 K.

thermal energy is also the function of temperature, therefore we plot the graph between temperature and thermal energy for direct vision of temperature dependence of thermal energy, we find a very close agreement with generalized data based on thermal pressure's experimental data [1]. Thus the results obtained by Eq. (24) show the consistency with experimental data and Eq. (25) as reflected from Figs. 3 and 4 for NaCl and KCl, respectively. It is also found that the plots between thermal energy and isothermal bulk modulus show linearity for the solids under study as it is clear from Figs. 5 and 6 for NaCl and KCl, respectively. It is because of thermal pressure and isothermal bulk modulus show the linearity at high temperatures [6]. And the thermal energy shows the linearity with thermal pressure. So the thermal energy shows the linearity with the isothermal bulk modulus.

4. Conclusions

In the present study, we present thermal energy for NaCl, KCl under varying conditions of temperature and volume from room temperature to their melting temperatures at $P = 1$ bar or 10^5 Pa. The results obtained in the present study are compared with available experimental data. It is found that the formulation is valid and present good agreement with the available experimental data. It is also found that E_{th} versus T plots show linear nature for both solids. And present study also discloses that thermal energy shows linearity with isothermal bulk modulus. The predicted data may be used to study thermal properties for solids.

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