A Comparative Study of Equations of State for Gruneisen Parameter (ϒ) with NaCl as sample

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ABSTRACT: The analysis of theoretical investigation of thermodynamic parameters has been proved of a great importance in the study of thermodynamic behavior of solids. The thermodynamic behavior of crystal can be fruitfully studied in terms of Gruneisen parameter (ϒ) as this parameter is related to thermodynamic quantities like bulk modulus, pressure, volume etc. Some efforts have been made in this direction but they are limited to few crystals upto very small range of pressure and temperature.

Keywords: Gruneisen parameter, Equation of state, Bulk Modulus

Introduction

In order to understand the thermodynamic behaviour of solids it is desirable to investigate the pressure and temperature dependence of Gruneisen parameter [1,2]. Dhoble and Verma [3,4] have shown on the basis of thermodynamic analysis that isothermal Anderson parameter can be expressed in terms of constant pressure and constant volume temperature derivatives of thermal expansion coefficient. Yamamoto *et al* [5] and Anderson and Yamamoto [6] presented an experimental method for determination of temperature variation of these parameters. Kumar and Upadhyay [7] develop a method based on interionic potential model which considers (i) the long-range electrostatic interactions in terms of Medelung's energy (ii) the short range overlap repulsive energy between nearest neighbours and next nearest neighbours by adopting the analytical potential form derived by Harrison [8] and on the basis of quantum mechanical considerations and (iii) the Van-der-waals (vdW) dipole-dipole and dipole quadrapole interactions evaluated from the Kirkwood-Muller formulae as reviewed by Shanker and Agrawal [9].

The basic definitions of γ can be found in literature [6]. Slater [10] suggested a method for calculating γ from the theory of elasticity. These expressions for vibrational velocities are valid only when the solid is under no external pressure. Dugdale and Mac-Donald [11] obtained a more general expression for γ by including the effect

of pressure. These theories do not take into account the variation of poisson's ratio with volume . Vaschenko and Zubarev have developed a formulation for γ using the free volume theory. Megault and Romain [12] proposed a unification of these theories by considering the volume dependence of Poisson'' ratio. Following their approach we can express γ by a common formula which reads as

$$\gamma = -\frac{(4-3x)}{6} - \frac{V}{2}\frac{d^2(PV_x)/dV^2}{d(PV_x)/dV} \qquad (1)$$

where P is pressure, V is volume and x is the parameter, which takes the value o in Slater's theory, 0.66 in Dugdale and Mac Donald's theory and 1.33 in free volume theory.

Theory Adopted And Calculation

Thus in order to evaluate γ with the help of equation (1) we need the derivations of P with V that is dP/dV, d²P/dV² and d³P/dV³. These derivatives are directly related to the derivatives of lattice potential energy [13] and can be estimated using the following expression based on interionic potential model considered in the present study.

$$W = -\frac{\alpha_M e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + \emptyset_{rep} \qquad (2)$$

where W is lattice potential energy and the first ferm on right hand side of equation (2) is electrostatic coulomb energy with α_M as Medelung's constant e is the electron charge. The second and third terms are vdW dipole-dipole and dipole-quadrapole energies. Last term is the overlap

repulsive energy. Values of C and D have been calculated using the Kirkwood-Muller formulae which are superior to all other existing formulae [9]. The overlap repulsive energy can be written as follows [14].

$$\phi_{rep} = \frac{6\,n_0\,n^2}{2\,m}\,[\overline{\mu}^3\,r\,\exp(-k\,\overline{\mu}\,r)$$

$$+ \sqrt{2}\,\mu^3{}_1\,r\,\exp(-\sqrt{2}\,k\,\mu_1\,r)$$ (3)

$$+ \sqrt{2}\,\mu^3{}_2,\,r\,\exp(-\sqrt{2}\,k\,\mu_2\,r)]$$

where h is Planck's constant divided by 2π, m the mass of electron and μ the arithmetic average of μ_1 and μ_2 for the cation and anion. The values of μ_1 and μ_2 can be calculated by the relation.

$$\mu^2 = -\frac{2m\,\varepsilon_i}{n}$$ (4)

where ε_i is the valence state energy of ions.

The calculations of γ and other thermodynamic parametrers depend sensitively on the values of x. According to the different theories of γ [11 ,12] the value of x should remain between 0 and 133. We have determined the value of x to fit the experimental values of γ [16, 4] at atmospheric pressure and room temperature for each crystal. It is interesting to see from Table 1 that the values of x thus determined range between 0 and 1.33 and are therefore consistent with the theories of γ. In further calculations we have assumed that x does not change with pressure and temperature. The good agreement between calculated and experimental values reveals the validity of this assumption.

Table -1 Values of input parameters for NaCl

Crystal	x	n_0	k	μ_1(A^0)$^{-1}$	μ_2(A^0)$^{-1}$	C (10^{-60} erg cm^6)	D(10^{-76} erg cm^6)
NaCl	o.950	16.60	1.39	3.087	1.799	561	455

The thermodynamic parameters γ, q can be calculated at higher pressures and higher temperatures following the method described in previous section using the parameters given in Table 12. Such calculations can be performed for all crystals listed in Table 1. However, we are reporting the results only for NaCl for which the experimental data are available [18,5] so that a direct comparison can be made in Table 2 . There is good agreement between calculated values and available experimental data.

TABLE – 2 Thermodynamic parameters for NaCl , temperature T (in K) and pressure P (in kbar) Experimental values are given in parentheses. Melting temperature 1073 K and transition pressure 283 kbars.

T/P	298		373		473		573		773	
	γ	q	γ	q	γ	q	γ	q	γ	q
0	1.61	1.32	1.63	1.35	1.66	1.30	1.69	1.27	1.75	1.23
	(1.61)	1.02	(1.63)	1.18	(1.66)	1.17	(1.68)	1.00	(1.65)	1.05
5	1.50 (1.50)	1.38	1.56	1.37	1.60	1.35	1.65	1.28	1.66	1.26
10	1.48 (1.49)	1.44	1.0	1.40	1.55	1.38	1.60	1.34	1.62	1.31
20	1.43 (1.44)	1.50	1.48	1.45	1.50	1.40	1.54	1.39	1.57	1.36
30	1.38 (1.40)	1.56	1.45	1.49	1.47	1.47	1.50	1.45	1.53	1.43
40	1.34	1.58	1.40	1.55	1.44	1.51	1.50	1.86	1.47	1.49
50	1.31	1.60	1.36	1.57	1.40	1.60	1.42	1.59	1.43	1.54
100	1.20	1.66	1.30	1.63	1.34	1,62	1.39	1.61	1.40	1.60
200	1.04	1.89	1.10	1.80	1.23	1.75	1.73	3.56	1.30	1.72
283	0.96	2.01	1.01	1.92	1.15	1.84	1.20	1.81	1.23	1.79

It is noted from Table 2 that γ decreases with increasing pressure and increase with increasing temperature, whereas q increases with increasing pressure and decreases with increasing temperature. Such a trend of variation is in agreement with the results obtained by Kumari and Dass [15] and Dhoble and Verma [3, 4]. Equations used in Table 2 for calculations are:

$$\gamma = -\frac{(4-3x)}{6} - \frac{V}{2}\,\frac{d^2(PV_x)/dV^2}{d(PV_x)/dV}$$ (5)

$$\delta_T = \frac{dB_T}{dP} + q - 1 \qquad (6)$$

$$\delta_S = \delta_T - \gamma \qquad (7)$$

$$q = \frac{V}{\gamma} \cdot \frac{d\gamma}{dV} \qquad (8)$$

Hui and Bao [19] have derived an expression Υ for as follows.

From equation

$$q = \left[\frac{\partial \ln\gamma}{\partial \ln V}\right]_T \qquad (9)$$

and

$$q = q_0\,\eta^n \qquad (10)$$

we get,

$$\gamma = \gamma_0 \exp\left[\,(q_0/n)\,(\eta^n - 1)\right] \qquad (11)$$

The compression η as a function of pressures can be calculated by equation of state for condensed matter. For alkali metals, the Birch equation is believed to be one of the best .

$$P\,(T_R, x) = (3/2)\,K_T\,(O,\,T_R)\,(x^{-7} - x^{-5})$$

$$\underline{x}\,[1 + 3/4\,\{K^I_T\,(O,\,T_R) - 4\}\,(x^{-2} - 1)] \qquad (12)$$

$K_T\,(0,\,T_R)$ and $K'_T\,(0,\,T_R)$ have the same meaning as in equation

$$\gamma = \gamma_0 = \left[1 + \frac{K^1(O,T_R)P}{K(O,T_R)}\right]^{-q/K'(O,T_R)} \qquad (13)$$

and $x = \eta^{1/3}$.

For Li, Na and K at $T_R = 298$ K, $K^1(0,\,T_R)$ and K_T' $(0,\,T_R)$ are chosen the same as those in Ref. [15]. The experimental values of γ are from Ref. [17], so the values of q_0 and n can be obtained by fitting the experimental data on the Gruneisen parameter γ under different pressure. Table 14 gives the calculated values of q_0 and n for Li, Na and K respectively. Combining this with equations 66-68, we calculate the Gruneisen parameter (γ_{cal}) and the second Gruneisen parameter in Table 15

Table – 3

The values of q_0 and n at 298 K.

	Li	Na	K
q_0	1.218	1.574	1.509
n	1.0	6.4	0.8

Table – 4 Volume dependence of Gruneisen parameter of Na AT 298 K (RMSD)

P (kbar)	Na	
	γ_{exp}	γ_{real}
0	1.216	1.140
5	1.050	1.043
10	1.000	.995
15	.980	.967
20	.960	.949
25	.940	.936
30	.940	.936
RMSD	**0.028**	

At P = 0, T = 298 K for Li, Na, K, q = 1.220, 1.574, 1.509 respectively. This is quite similar to Boehler's results [17]. Besides $q = q_0\,\eta^n$ decreases with pressure, in a manner different from that reported by Kumari and Dass [15] are well shown to agree well with experimental data, this work is still a little bit better than them. From the definition of the bulk modulus

$$K = -V\left[\frac{\partial P}{\partial V}\right]_T$$

the Murnaghan equation is derived

$$P = \frac{K\,(O,T_R)}{K'(O,T_R)}\left[\eta^{-K(O,T_R)} - 1\right] \qquad (14)$$

Substituting equation (14) to equation (13), we get

$$\gamma = \gamma_0\,\eta^q \qquad (15)$$

This is just the often assumed power law equation (15). When the pressure is not too high, equation (11) changes into

$$\gamma = \gamma_0 \left[1 - \frac{q_0}{n}\right] + \frac{q_0}{n} \eta^n \qquad (16)$$

If $q_0 = n$, equation (16) changes into equation (15). So equation (11) is applicable to wider pressure ranges than equation (13). Moreover, when the pressure tends towards infinity, the value of γ given by equation (11)

$$\gamma = \gamma_0 \exp\left[\frac{q_0}{n}\right] \qquad (17)$$

which is not zero as equation (13,15). This result seems more close to reality .

Conclusion

Thus we conclude that for NaCl there is good agreement between calculated values and available experimental data. It is noted that Υ decreases with increasing pressure and increase with increasing temperature, whereas q increases with increasing pressure and decreases with increasing temperature. Such a trend of variation is in agreement with the results obtained by Kumari and Dass [57] and Dhoble and Verma [58,59].

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