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Thermal effect and equation of state in solids

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Abstract. In the present paper, an attempt has been made to include the thermal effect into an isothermal equation of state using the Debye approximation representing volume as a function of pressure. The calculations are done in case of NaCl, CsCl, Mo, and W. The present calculations are in good agreement with the reported results.

Keywords. Thermal effect; equation of state; Debye approximation.

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1. Introduction

Two types of isothermal equation of state (EOS) are available in the literature. In one, the pressure is expressed as a function of volume, i.e. $P = f(V)$. The second in which the volume is expressed as a function of pressure, i.e., $V = f(P)$. The thermal effect into the first type of EOS due to the Debye approximation is very well known [1,2], somehow no attempt has been made to include the thermal effect due to the Debye approximation into the second type of EOS. The possible reason may be that (i) the pressure dependence of γ is not known and (ii) the pressure dependence of the Debye temperature, Θ, is not known. But at present the pressure dependence of γ and Θ are available in the literature. Therefore, the aim of the present paper is to include the thermal effect into a second type of isothermal EOS to make it as temperature dependent EOS.

2. Theory

An EOS expressing the volume in terms of pressure really corresponds to the experimental situation and hence such EOS is considered to be better than the other form of EOS, i.e., expressing pressure in terms of volume. This goal is achieved by differentiating free energy [3] of the solids with respect to pressure considering the Debye temperature a pressure dependent, $\Theta(P)$. The EOS of a solid, in Debye approximation, has been found as

$$V(P,T) = V_P + \frac{\gamma(P,T)}{B_T(P,T)}\left[\frac{9}{8}nR\Theta + 3nRTD(X)\right] \tag{1}$$

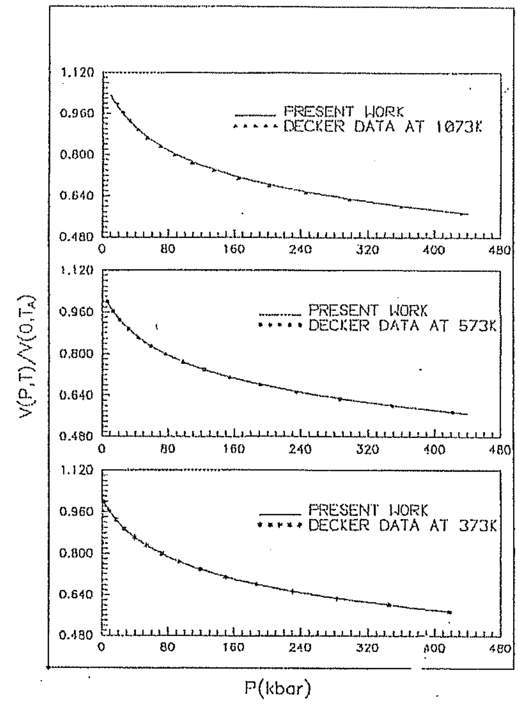

Figure 1. Comparison of $V(P,T)/V(0,T_A)$ with pressure at different temperatures for NaCl.

where

$$D(X) = \frac{3}{X^3}\int_0^X \frac{X^3}{e^X - 1}\mathrm{d}X \quad \text{and} \quad X = \frac{\Theta}{T}$$

V_P, Θ, n and γ denote, respectively, the volume in static lattice, the Debye temperature, the number of atoms in the unit cell and the thermodynamic Gruensien parameter. The second term, i.e., zero point volume can be neglected because of its smallness.
Equation (1) can also be written as

$$V(P,T) = V(P,T_A) + \frac{\gamma(P,T_A)}{B_T(P,T_A)}\left[E(\Theta_T) - E(\Theta_{T_A})\right]. \tag{2}$$

In obtaining eq. (2), we make use of the following assumption:

$$\frac{\gamma(P,T)}{B_T(P,T)} \simeq \frac{\gamma(P,T_A)}{B_T(P,T_A)} \tag{3}$$

Expression for the variation of $\gamma(P,T_A)$ and $\Theta(P,T_A)$ with pressure have been taken from Kumari and Dass [4] and are given below

$$\gamma(P,T_A) = \gamma(0,T_A) - \mu P \tag{4}$$

$$\Theta(P,T_A) = \Theta(0,T_A)\left[1+\frac{B'_T(0,T_A)}{B_T(0,T_A)}P\right]^{+\gamma(0,T_A)/B'_T(0,T_A)} \tag{5}$$

where μ has been taken as an adjustable parameter.

Table 1. Input data.

Solids	NaCl	CsCl	Mo	W
$B_T(0,T_A)$ (kbar)	240.14 [7]	172.51 [7]	2709.2 [5]	3138.04 [5]
$B'_T(0,T_A)$	4.54 [7]	4.96 [7]	3.58 [5]	3.68 [5]
$\gamma(0,T_A)$	1.6275 [6]	1.99 [6]	1.58 [2]	1.65 [2]
$\Theta(0,T_A)$ (K)	279.0 [6]	151.0 [6]	411.0 [2]	340.0 [2]
$\mu(X10^{-3}$ kbar$^{-1})$	2.2	1.2	0.175	0.175
$V(0,T_A)$ (cm^3/mole)	26.99	42.18	9.39	9.55
Temperature range (K)	273.0–1073.0	273.0–1073.0	293.0–7605.0	293.0–6905.0
Pressure range (kbar)	0.0–320.0	0.0–432.0	0.0–3000.0	0.0–3000.0

Table 2. Comparison of density as a function of pressure and temperature for Mo and W.

Mo				W		
P (Gpa)	T(K)	ρ (gm/cm^3) From [2]	ρ (gm/cm^3) Calculated	T(K)	ρ (gm/cm^3) From [2]	ρ (gm/cm^3) Calculated
0.0	293.0	10.215	10.215	293.0	19.256	19.256
10.0	311.0	10.577	10.573	309.0	19.846	19.841
20.0	338.0	10.906	10.901	332.0	20.388	20.383
30.0	378.0	11.208	11.205	336.0	20.891	20.887
40.0	435.0	11.489	11.487	413.0	21.360	21.358
50.0	510.0	11.752	11.751	477.0	21.802	21.801
60.0	604.0	11.999	11.998	556.0	22.219	22.219
70.0	716.0	12.233	12.232	652.0	22.614	22.615
80.0	847.0	12.455	12.454	765.0	22.991	22.991
90.0	996.0	12.666	12.665	894.0	23.351	23.350
100.0	1163.0	12.868	12.866	1040.0	23.695	23.694
110.0	1347.0	13.062	13.058	1202.0	24.026	24.023
120.0	1549.0	13.248	13.243	1380.0	24.345	24.340
130.0	1767.0	13.427	13.420	1573.0	24.652	24.645
140.0	2002.0	13.599	13.592	1582.0	24.948	24.939
150.0	2252.0	13.766	13.757	2006.0	25.235	25.224
160.0	2517.0	13.927	13.917	2244.0	25.513	25.500
170.0	2798.0	14.083	14.072	2496.0	25.782	25.768
180.0	3092.0	14.235	14.223	2762.0	26.044	56.029
190.0	3401.0	14.382	14.370	3042.0	26.298	26.282
200.0	3723.0	14.525	14.513	3334.0	26.546	26.530
210.0	4058.0	14.664	14.652	3639.0	26.787	26.771
220.0	4406.0	14.800	14.789	3957.0	27.022	27.007
230.0	4766.0	14.932	14.922	4286.0	27.251	27.238
240.0	5139.0	15.061	15.053	4628.0	27.475	27.465
250.0	5523.0	15.187	15.181	4980.0	27.693	27.687
260.0	5918.0	15.310	15.307	5344.0	27.907	27.905
270.0	6324.0	15.430	15.430	5719.0	28.116	28.119
280.0	6741.0	15.548	15.552	6104.0	28.320	28.330
290.0	7168.0	15.663	15.672	6499.0	28.521	28.537
300.0	7605.0	15.776	15.790	6905.0	28.717	28.742

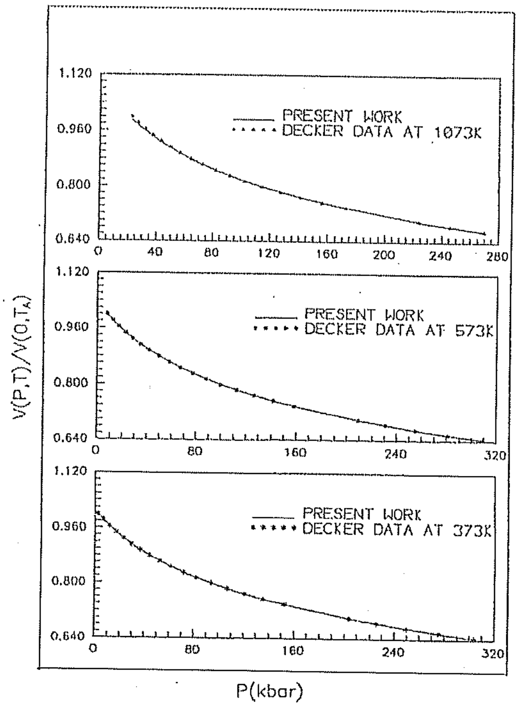

Figure 2. Comparison of $V(P,T)/V(0,T_A)$ with pressure at different temperatures for CsCl.

As far as $V(P,T_A)$ and $B_T(P,T_A)$ are concerned, we have been able to reduce the three parameter EOS [5] into two parameter EOS as given below

$$\frac{V(P,T_A)}{V(0,T_A)} = [(1+\beta)\exp(ZP) - \beta]^{-1/\eta} \tag{6}$$

$$B_T(P,T_A) = B_T(0,T_A)[1+\beta(1-\exp(-ZP))] \tag{7}$$

where

$$\beta = 3B'_T(0,T_A), \quad \eta = [3B_T(0,T_A)+1]/3 \quad \text{and} \quad Z = [3B_T(0,T_A)]^{-1}.$$

3. Calculations and results

Thus, it is clear from eqs (2)–(8) that $V(P,T)$ can be calculated once the value of $B_T(0,T_A)$, $B'(0,T_A), \gamma(0,T_A)$, μ and $\Theta(0,T_A)$ become known. The best fitted value of μ and other relevant parameters needed for calculation are reported in table 1. By making use of eq. (2) and taking the values of relevant parameters from table 1, the volume is computed for NaCl, CsCl, Mo, and W as a function of pressure and temperature.

The calculated values of $V(P,T)/V(0,T_A)$ for NaCl and CsCl are compared with the available data of Decker [6] in figures 1 and 2. The agreement is very good as the discrepancy lies within ± 1.0% in the whole range of pressure and temperature.

The computation of density is done with the help of eq. (2) for Mo, and W. The results are compared with the Hugonoit result of Hixon and Fritz [2] in table 2. The discrepancy is ± 0.087% for Mo and ± 0.09% for W in the whole range of pressure and temperature. Thus, very good agreement is observed.

Hence, it can be concluded that the inclusion of thermal effect into an isothermal EOS is quite successful in representing the volume compression as a function of pressure and temperature.

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