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The Grünesian Parameter And Its Higher Order Derivatives For Some Binary Solids

K. Dharmendra[1] and P.K. Singh[2*]

[1]Department of Physics, Karm Kshetra P.G. College, Etawah 206001, India
[2]Department of Physics, Shri Sadguru Saibaba Science & Commerce College, Ashti
*Corresponding author Email:pramod0002000@yahoo.com

Abstract

We have formulated an expression for the Grüneisen parameter gamma in terms of the ratio of pressure and bulk modulus. The generalized free volume formula reveals that Gamma depends on pressure, bulk modulus and its pressure derivative. These quantities have been predicted using the Holzapfel adapted polynomial of second order (AP2) equation of state (EOS). We have derived expressions for the second order and the third order Grüneisen parameter in terms higher order pressure derivatives of bulk modulus. The results have been obtained for the Grüneisen parameter and its volume derivatives for some binary solids viz. NaCl, NaF, LiF, MgO, CaO, SiC and CaF_2. The infinite pressure behavior of thermoelastic parameters has been discussed using the thermodynamic constraints.

Keywords: Grüneisen parameter, Pressure derivatives of bulk modulus, Holzapfel equation of state, Binary solids, Infinite pressure behavior.

1. INTRODUCTION

The Grüneisen parameter γ is related to thermoelastic properties of materials [1-3]. The pressure derivatives of γ play a central role in predicting the thermal behavior, equation of state, and melting at high pressures [4-7]. The free volume theory of gamma [8] has been generalized [6, 9] to obtain γ as a function of pressure P, bulk modulus K and pressure derivative of bulk modulus $K' = dK/dP$. This generalized free-volume formula can be written as

$$\gamma = \frac{\frac{K'}{2} - \frac{1}{6} - \frac{f}{3}\left(1 - \frac{P}{3K}\right)}{1 - 2f\frac{P}{3K}} \tag{1}$$

Where K is the bulk modulus at pressure P, and f is the free volume parameter. Different formulations [10-12] were developed forγ using the different values of parameter f.

In order to investigate higher order pressure derivatives of the Grüneisen parameter γ with the help of Eq.(1), we need to know the pressure derivatives of the parameter f such as df/dP and d^2f/dP^2. However, these derivatives are highly uncertain because of the values of f which differ significantly from each other for different formulations. Shanker et al [13] have developed a formulation for gamma by considering a relationship between reciprocal γ and the ratio P/K. It has been shown recently Singh and Dharmendra [14] that the quadratic equation for $K' = dK/dP$ in P/K is more appropriate than a linear relationship. Since the variations of γ and K' with increasing pressure are very similar, we have used in the present study a quadratic equation for reciprocal γ in P/K. We have derived expressions for the second order

Grüneisenparameter γ and the third order Grüneisen parameter λ. Values of γ, q and λ have been determined using the results based on the adapted polynomial of second order (AP2) equation of state (EOS) [15, 16].

II. METHOD OF ANALYSIS AND RESULTS

Values of P, K, K' KK'' and K^2K''' for seven materials viz. NaCl, NaF, LiF, MgO, CaO, SiC and CaF_2 have been calculated using the expressions based on the Holzapfel AP2 EOS given in reference [14]. The input parameters used in calculations are given in Table 1 and the results in Table 2.

In the present study we propose the following expression for the reciprocal gamma

$$\frac{1}{\gamma} = A_1 + A_2\left(\frac{P}{K}\right) + A_3\left(\frac{P}{K}\right)^2 \tag{2}$$

At atmospheric pressure P=0, Eq.(2) gives

$$A_1 = \frac{1}{\gamma_0} \tag{3}$$

Now differentiating Eq.(2) with respect to volume we get

$$-\frac{1}{\gamma^2}\frac{d\gamma}{dV} = A_2\left[\frac{1}{K}\frac{dP}{dV} - \frac{P}{K^2}\frac{dK}{dV}\right] + 2A_3\left(\frac{P}{K}\right)\left[\frac{1}{K}\frac{dP}{dV} - \frac{P}{K^2}\frac{dK}{dV}\right] \tag{4}$$

Using the following relationships

$$q = \frac{V}{\gamma}\frac{d\gamma}{dV} \tag{5}$$

$$K = -V\frac{dP}{dV} \tag{6}$$

and

$$K' = \frac{dK}{dP} = -\frac{V}{K}\frac{dK}{dV} \tag{7}$$

Then we get

$$\frac{q}{\gamma} = \left(A_2 + 2A_3\frac{P}{K}\right)\left[1 - K'\frac{P}{K}\right] \tag{8}$$

At P=0, $q = q_0$, $\gamma = \gamma_0$

$$A_2 = \frac{q_0}{\gamma_0} \tag{9}$$

Anderson [1] has discussed at length that $q_0 = 1$ is an appropriate choice for different types of materials. We have therefore taken $q_0 = 1$ in present calculations. Thus we can write

$$A_1 = A_2 = \frac{1}{\gamma_0} \tag{10}$$

Now differentiating Eq.(8) with respect to volume we get

$$\frac{q\lambda}{\gamma}-\frac{q^2}{\gamma}=2A_3\left(1-K'\frac{P}{K}\right)^2+\left(A_2+2A_3\frac{P}{K}\right)\left[KK''\frac{P}{K}+K'\left(1-K'\frac{P}{K}\right)\right] \quad (11)$$

where λ is the third order Grüneisen parameter given below [13]

$$\lambda=\frac{V}{q}\left(\frac{dq}{dV}\right) \quad (12)$$

Dividing Eq.(11) by Eq.(8) we get

$$\lambda-q=\frac{KK''\left(\frac{P}{K}\right)}{1-K'\left(\frac{P}{K}\right)}+K'+\frac{2A_3\left(1-K'\frac{P}{K}\right)}{A_2+2A_3\left(\frac{P}{K}\right)} \quad (13)$$

Values of A_3 are determined using infinite pressure constraint due to Knopoff [17]

$$\left(\frac{P}{K}\right)_\infty=\frac{1}{K'_\infty} \quad (14)$$

Now writing Eq.(2) at infinite pressure we have

$$\frac{1}{\gamma_\infty}=A_1+A_2\left(\frac{P}{K}\right)_\infty+A_3\left(\frac{P}{K}\right)_\infty^2 \quad (15)$$

Eqs. (14) and (15) yield the following relationship with the help of Eq. (10)

$$\frac{1}{\gamma_\infty}=\frac{1}{\gamma_0}+\frac{1}{\gamma_0 K'_\infty}+\frac{A_3}{K'^2_\infty} \quad (16)$$

Values of A_3 have been calculated with the help of Eq. (16). Using the parameters given in Table 1 and the results in Table 2,we have computed values of γ, q and λ for seven binary compounds given in Figures 1, 2 and 3.

III. DISCUSSION AND CONCLUSIONS

It is found that γ, q and λ all decrease with the increase in pressure. In the limit of infinite pressure or extreme compression (V→0), the first orderGrüneisen parameterγ and the third order Grüneisen parameter λ remain positive and finite such that $\gamma_\infty=1/2$ [18] and $\lambda_\infty=1/3$ [19]. On the other hand, the second order Grüneisen parameter q in the limit of extreme compression, i.e $q_\infty\to 0$. This can be verified from Eq. (8) for q using the Knopoff constraint given by Eq.(14). The third order Grüneisen parameter λin the limit of infinite pressure, Eq.(13) is reduced to the following formula

$$\lambda_\infty=K'_\infty+\frac{KK''\left(\frac{P}{K}\right)}{1-K'\left(\frac{P}{K}\right)} \quad (17)$$

It should be noted that Eq.(17) for λ_∞ give above is in agreement with the relationship derived earlier by Shanker et al [20]. The results obtained in the present study are thus consistent with the thermodynamic constraints for materials in the limit infinite pressure.

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Table 1: Input parameters appearing in the Holzapfel AP2 equation of state for some binary solids at room temperature and atmospheric pressure.

Parameters	NaCl	NaF	LiF	MgO	CaO	SiC	CaF2
K_0 (GPa)	24.0	46.5	66.5	162	111.0	241	81.7
K_0'	5.35	5.28	5.30	4.15	4.85	2.84	5.22
γ_0	1.59	1.72	1.63	1.54	1.35	1.06	1.90
A1=A2	0.629	0.581	0.613	0.649	0.741	0.943	0.526
A3	2.76	2.972	2.829	2.67	2.263	1.363	3.216

Table 2: Results obtained from the Holzapfel AP2 EOS for pressure derivatives of bulk modulus for

NaCl

V/V0	P (GPa)	K (GPa)	K'	KK"	K^2K'''
1.00	0.00	24.00	5.35	-9.10	99.74
0.95	1.41	31.24	4.95	-6.97	68.05
0.90	3.34	40.44	4.61	-5.47	48.08
0.85	5.98	52.20	4.33	-4.37	34.94
0.80	9.59	67.37	4.09	-3.55	25.97
0.75	14.55	87.14	3.89	-2.92	19.66
0.70	21.43	113.2	3.70	-2.42	15.11
0.65	31.06	148.0	3.54	-2.03	11.76
0.60	44.72	195.3	3.39	-1.71	9.25

NaF

V/V0	P (GPa)	K (GPa)	K'	KK"	K^2K'''
1.00	0.00	46.50	5.28	-9.24	101.16
0.95	2.73	60.29	4.87	-7.06	68.72
0.90	6.44	77.69	4.53	-5.53	48.37
0.85	11.50	99.81	4.25	-4.41	35.03
0.80	18.38	128.1	4.01	-3.57	25.95
0.75	27.79	164.8	3.80	-2.93	19.58
0.70	40.76	212.8	3.61	-2.43	15.01
0.65	58.80	276.3	3.45	-2.03	11.65
0.60	84.22	362.0	3.30	-1.71	9.13

LiF

V/V0	P (GPa)	K (GPa)	K'	KK"	K^2K'''
1.00	0.00	66.50	5.30	-9.90	110.78
0.95	3.90	86.25	4.86	-7.49	74.11
0.90	9.22	111.0	4.50	-5.81	51.51
0.85	16.43	142.4	4.21	-4.60	36.90
0.80	26.24	182.3	3.96	-3.71	27.09
0.75	39.60	233.6	3.74	-3.02	20.28
0.70	57.95	300.4	3.55	-2.49	15.43
0.65	83.35	388.3	3.38	-2.07	11.89
0.60	119.0	505.9	3.23	-1.74	9.26

MgO

V/V0	P (GPa)	K (GPa)	K'	KK"	K^2K'''
1.00	0.00	162.0	4.15	-4.88	40.85
0.95	9.24	199.3	3.93	-3.98	30.63
0.90	21.22	245.0	3.73	-3.28	23.36
0.85	36.80	301.7	3.56	-2.73	18.06
0.80	57.18	372.6	3.41	-2.29	14.13
0.75	84.04	462.2	3.27	-1.93	11.17
0.70	119.8	576.7	3.15	-1.64	8.89
0.65	167.8	725.2	3.04	-1.40	7.13
0.60	233.4	920.9	2.93	-1.19	5.74

CaO

V/V0	P (GPa)	K (GPa)	K'	KK"	K^2K'''
1.00	0.00	111.0	4.85	-7.54	75.30
0.95	6.44	141.1	4.51	-5.90	52.97
0.90	15.05	178.6	4.22	-4.70	38.33
0.85	26.57	225.7	3.98	-3.80	28.38
0.80	42.01	285.5	3.77	-3.12	21.41
0.75	62.82	362.0	3.59	-2.58	16.40
0.70	91.10	461.0	3.43	-2.16	12.72
0.65	129.9	591.0	3.28	-1.81	9.97
0.60	183.9	764.3	3.15	-1.53	7.88

SiC

V/V0	P (GPa)	K (GPa)	K'	KK"	K^2K'''
1.00	0.00	241.0	2.84	-1.64	9.87
0.95	13.30	278.2	2.76	-1.40	8.11
0.90	29.51	322.4	2.69	-1.19	6.66
0.85	49.42	375.4	2.63	-1.01	5.48
0.80	74.08	439.5	2.57	-0.86	4.50
0.75	104.9	518.0	2.52	-0.72	3.68
0.70	143.9	615.5	2.48	-0.61	3.01
0.65	194.0	738.3	2.44	-0.51	2.44
0.60	259.2	895.8	2.40	-0.42	1.96

CaF2

V/V0	P (GPa)	K (GPa)	K'	KK"	K^2K'''
1.00	0.00	81.70	5.22	-9.16	99.57
0.95	4.79	105.6	4.81	-7.00	67.70
0.90	11.29	135.7	4.47	-5.48	47.68
0.85	20.10	173.8	4.19	-4.37	34.53
0.80	32.06	222.4	3.96	-3.54	25.58
0.75	48.38	285.2	3.75	-2.91	19.30
0.70	70.78	367.0	3.57	-2.41	14.79
0.65	101.8	475.0	3.40	-2.01	11.47
0.60	145.4	620.0	3.26	-1.69	8.98

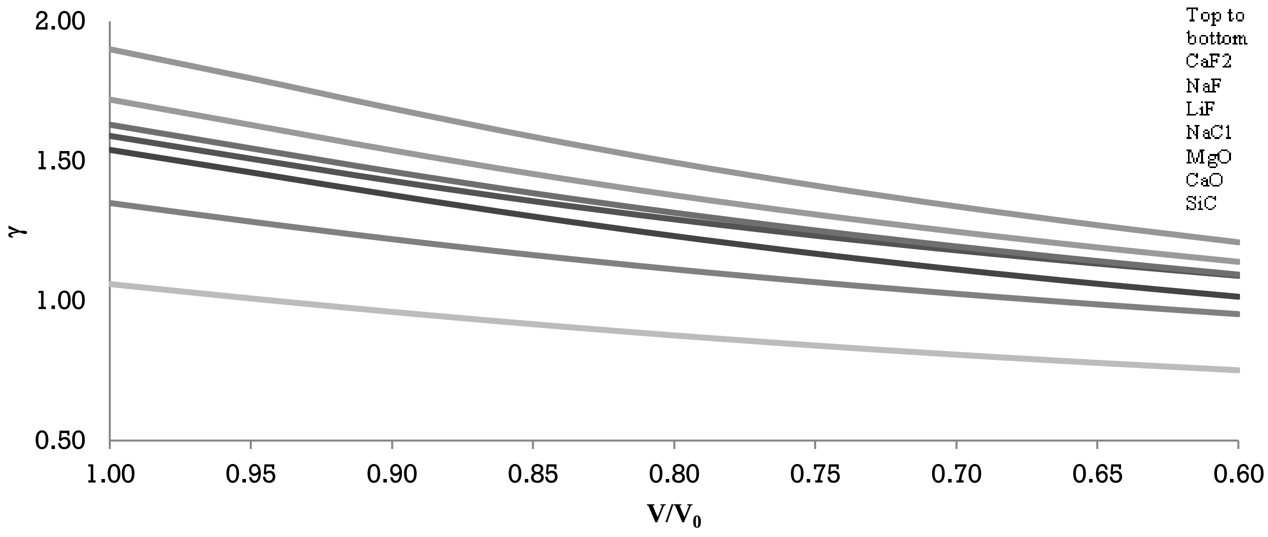

Figure 1- Plots between theGrüneisen parameter γ versus V/V_0.

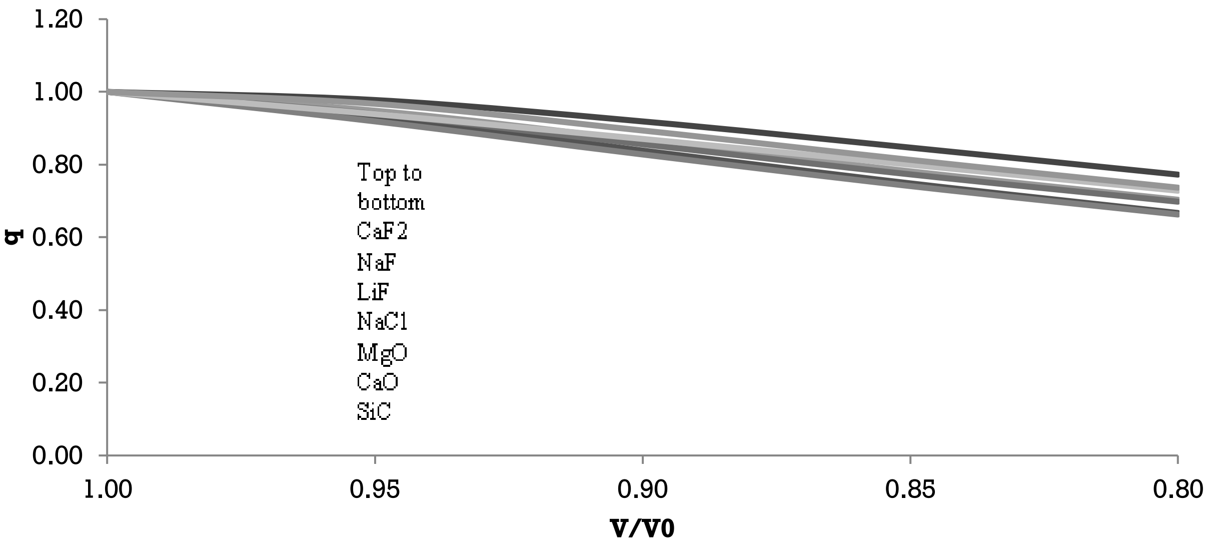

Figure 2- Plots between thesecond order Grüneisen parameter q versus V/V_0.

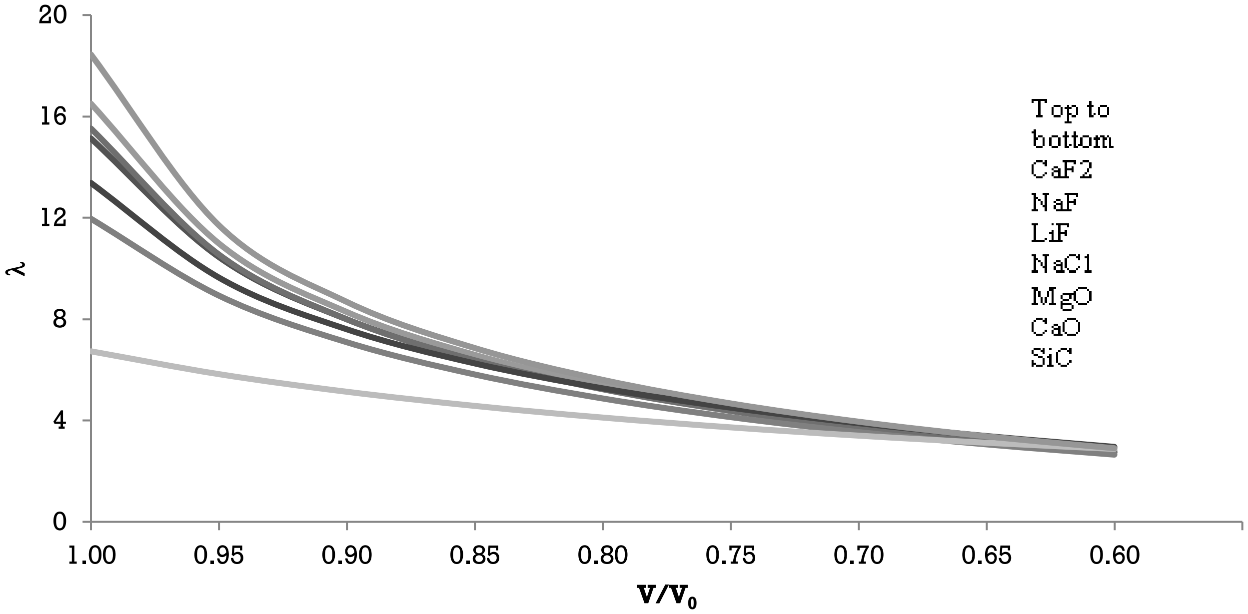

Figure 3- Plots between thethird order Grüneisen parameter λ versus V/V_0.