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Research Article

GRÜNEISEN PARAMETER AND ITS HIGHER DERIVATIVES FOR Pt, Fe, V AND Nb USING EQUATIONS OF STATE

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ABSTRACT

We have calculated the high pressure properties, Grüneisen parameter and its volume derivatives of metals Platinum, Iron, Vanadium and Niobium using free volume theory. We have used some of the most reliable high pressure equation of state (EOS) to determine the thermo-elastic parameter and its higher order volume derivatives based on the generalized free volume theory. We have used two EOS`s (a) Stacey Reciprocal K-primed EOS, (b) Kushwah Logarithmic EOS to find the Grüneisen parameter and its volume derivatives for metals at different values of compression from (1.0 to 0.5). The results for thermo-elastic parameters show systematic variations.

INTRODUCTION

Foinr understanding the high pressure - high temperature behaviour of solids, it is necessary to have a reliable knowledge of pressure – volume – temperature relationships (Anderson, 1995). For this purpose an equation of state (EOS) can be used with the help of different approaches, one of them is based on the Mie – Grüneisen – Debye (MGD) model for evaluating the thermal effects in order to determine P –V relationships at high temperatures (Speziale *et al*., 2001; Dorogokupets and Dewaele, 2007 and Dorogokupets and Oganov, 2007). In the reduction of shock-wave data to isothermal data, the knowledge of pressure dependence of the Grüneisen parameter is very useful. Studies on equation of state (EOS) are of central importance for predicting thermo elastic properties of materials at high pressures (Anderson, 1995; Stacey and Davis, 2004 and Stacey, 2005).

The Grüneisen parameter (γ) provides a useful link between thermal and elastic properties (Kushwah *et al*., 2003; Shanker *et al*., 2009 and Kushwah and Bhardwaj, 2010). The Grüneisen parameter γ and its volume derivatives q and λ can be determined with help of pressure derivatives of bulk modulus (Shanker and Singh, 2005 and Shanker *et al*., 2009) using the free volume theory. The volume variation of Grüneisen parameter (γ) is very important in theoretical equation of state, geophysical models, ultrasonic measurements and melting of solids. The Grüneisen parameter (γ) has considerable appeal to geophysicists because it is an approximately constant, dimensionless parameter that varies slowly as a function of pressure and temperature (Rai *et al*., 2010 and Vashchenko and Zubarev, 1963). In the present study, we determine the Grüneisen parameter γ and its volume derivatives q and λ for metals Pt, Fe, V and Nb at different values of compression down to V/V_0 (1.0 to 0.5).

We have used the Stacey reciprocal K- primed (Stacey, 2000) and Kushwah generalized logarithmic EOS (Kushwah *et al*., 2007). These EOS have been found to satisfy thermodynamic constraints for material. The results have been found to good agreement with the stacey EOS (Kushwah *et al*., 2007 and Shrivastava, 2009). The free volume theory has been applied successfully by Holzapfel *et al*. (2001) to investigate the volume dependence of γ in case of different metals. The free volume theory is based on the fundamental relationship between thermal pressure and thermal energy and therefore it is applicable for metals.

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Theory

The most important parameters providing connection between thermal and elastic properties is the Grüneisen parameter (Anderson, 1995)

$$\gamma = \frac{\alpha K_T}{\rho C_V} = \frac{\alpha K_S}{\rho C_P} \tag{1}$$

Where α is the thermal expansivity, ρ is density, K_T and K_S are isothermal and adiabatic bulk moduli, C_V and C_P are specific heats at constant volume and constant pressure, respectively. The higher order Grüneisen parameters are defined as (Stacey, 2005 and Shanker and Singh, 2005)

$$q = \left[\frac{d\ln\gamma}{d\ln V}\right]_T = -\frac{K}{\gamma}\left[\frac{d\gamma}{dP}\right]_T \tag{2}$$

$$\lambda = \left[\frac{d\ln q}{d\ln V}\right]_T = -\frac{K}{q}\left[\frac{dq}{dP}\right]_T \tag{3}$$

According to the generalized free volume theory (Stacey and Davis, 2004 and Vashchenko and Zubarev, 1963), we have the following expression for the Grüneisen parameter

$$\gamma = \frac{(K'/2) - (1/6) - (f/3)\left(1 - (1/3)(P/K)\right)}{1 - 2f\,(1/3)(P/K)} \tag{4}$$

It can also be written as

$$\gamma = \frac{K'}{2} - \frac{1}{6} - \varepsilon$$

Where

K = bulk modulus
K' = first derivative of bulk modulus
K'' = second derivative of bulk modulus

$$\varepsilon = \frac{f\left(K - K'P\right)}{\left(3K - 2fP\right)} \tag{5}$$

The following expressions are obtained from the differentiation of eq. (4)

$$q\gamma = -\frac{KK''}{2} + K\frac{d\varepsilon}{dP} \tag{6}$$

and

$$\gamma q\left(q + \lambda\right) = \frac{K'KK''}{2} + \frac{K^2K'''}{2} - KK'\frac{d\varepsilon}{dP} - K^2\frac{d^2\varepsilon}{dP^2} \tag{7}$$

Where the pressure derivatives of ε obtained from eq. (5) as follows

$$\frac{d\varepsilon}{dP} = -\frac{\left[fK''P + \varepsilon\left(3K' - 2f\right)\right]}{\left(3K - 2fP\right)} \tag{8}$$

And

$$\frac{d^2\varepsilon}{dP^2} = -\frac{\left[fK'''P + fK'' + 3\varepsilon K'' + 2\left(3K' - 2f\right)\left(d\varepsilon/dP\right)\right]}{\left(3K - 2fP\right)} \tag{9}$$

$$q + \lambda = -K' - \left[\frac{\left(\frac{K^2K'''}{KK''}\right) - \left(\frac{2K}{K''}\right)\left(\frac{d^2\varepsilon}{dP^2}\right)}{1 - \left(\frac{2}{K''}\right)\left(\frac{d\varepsilon}{dP}\right)}\right] \tag{10}$$

Where

$$K'' = \frac{d^2K}{dP^2},\ K''' = \frac{d^3K}{dP^3}\ and\ \ \varepsilon = \frac{f\left(K - K'P\right)}{\left(3K - 2fP\right)} \tag{11}$$

Values of $d\varepsilon / dP$ and $d^2\varepsilon / dP^2$ appearing in eq.'s (6) and (7) can be determined by differentiating eq. (11) with respect to pressure P by taking a constant value of parameter f for different metals. It is evident from eq.'s (4)-(11) that the basic quantities we need for determining γ, q and λ at different pressures are the bulk modulus and its pressure derivatives up to third order. For this purpose we use two different equations of State. The equations of State used in the present study are given below

(a) Stacey reciprocal K-primed EOS[18]

$$\ln\left(\frac{V}{V_0}\right) = \frac{K_0'}{K_\infty'^2}\ln\left(1 - K_\infty'\frac{P}{K}\right) + \left(\frac{K_0'}{K_\infty'} - 1\right)\frac{P}{K} \tag{12}$$

The expression for bulk modulus K and higher order pressure derivatives of bulk modulus can be obtained by successive differentiation of eq. (12) which are given below:

$$K = K_0\left[1 - \frac{K_\infty' P}{K}\right]^{-K_0'/K_\infty'} \tag{13}$$

$$\frac{1}{K'} = \frac{1}{K_0'} + \left(1 - \frac{K_\infty'}{K_0'}\right)\frac{P}{K} \tag{14}$$

$$KK'' = \frac{K'^2}{K_0'}\left(K_\infty' - K'\right) = K'^2 + \left(1 - \frac{K_\infty'}{K_0'}\right)\left(1 - \frac{P}{K}K'\right) \tag{15}$$

$$K^2K''' = \frac{K'^3}{K_0'^2}\left(3K' - 2K_\infty' + K_0'\right)\left(K' - K_\infty'\right) = \frac{KK'K''}{K_0'}\left(2K_\infty' - K_0' - 3K'\right) \tag{16}$$

$$\left(\frac{K^2K'''}{KK''}\right)_\infty = -K_\infty' - \frac{K_\infty'^2}{K_0'} \tag{17}$$

(b) Kushwah logarithmic EOS[19]

$$Px^{K'_\infty} = B_1 \ln(2-x) + B_2 [\ln(2-x)]^2 + B_3 [\ln(2-x)]^3 \quad (18)$$

where

$$B_1 = K_0, \qquad B_2 = \frac{K_0}{2}\left(K'_0 - 2K'_\infty + 2\right),$$

and

$$B_3 = \frac{K_0}{6}\left(K_0 K''_0 + K'^2_0 + 3K'^2_\infty - 3K'_0 K'_\infty - 12K'_\infty + 6K'_0 + 6\right)$$

The constant B_1, B_2 and B_3 can be calculated by applying boundary conditions P=0, $V=V_0$. The expressions for bulk modulus K and higher order pressure derivatives of bulk modulus can be obtained by successive differentiation of eq. (18) which are given below:

$$K = K'_\infty P - \frac{x^{1-K'_\infty}}{(2-x)}\left[B_1 + 2B_2 \ln(2-x) + 3B_3 \{\ln(2-x)\}^2\right] \quad (19)$$

$$K' = 2K'_\infty - \frac{K'^2_\infty P}{K} + \frac{2}{2-x}\left[+\frac{K'_\infty P}{K} + \frac{x^{2-K'_\infty}}{K(2-x)}\left[B_2 + 3B_3 \ln(2-x)\right] - 1\right] \quad (20)$$

$$KK'' = -3K'^2_\infty - K'^2 + 3K'K'_\infty + \frac{K'_\infty P}{K}\left[K'^2_\infty - \frac{6K'_\infty}{(2-x)} + \frac{2(4-x)}{(2-x)^2}\right] + \frac{2}{(2-x)}\left[6K'_\infty - 3K' - \frac{(4-x)}{(2-x)}\right] + \frac{6B_3 x^{3-K'_\infty}}{K(2-x)^3} \quad (21)$$

$$K^2K''' = 3KK''\left[K'_\infty - K' - \frac{2}{(2-x)}\right] + K'_\infty\left(1 - \frac{PK'}{K}\right)\left[K'^2_\infty - \frac{6K'_\infty}{(2-x)} + \frac{2(4-x)}{(2-x)^2}\right] + \frac{2K'_\infty Px}{K(2-x)}\left[3K'_\infty - \frac{(6-x)}{(2-x)}\right] - \frac{2x}{(2-x)^2}\left[6K'_\infty - 3K' - \frac{(6-x)}{(2-x)}\right] + \frac{6B_3 x^{3-K'_\infty}}{K(2-x)^3}\left[K'_\infty - K' - \frac{6}{(2-x)}\right] \quad (22)$$

$$\left(\frac{K^2K'''}{KK''}\right)_\infty = -K'_\infty - 1$$

In Stacey and Kushwah logarithmic EOS, values of K'_∞ are substantially higher than 5/3. These both equations yield almost identical results. We compare the results γ, q *and* λ determine from the Stacey EOS with Kushwah logarithmic EOS.

We have thus studied the Grüneisen gamma and its higher order derivatives q and λ. These thermo-elastic parameters are directly related to the pressure derivatives of bulk modulus up to third order. The expressions based on the Stacey EOS and the Kushwah logarithmic EOS satisfy the infinite pressure conditions viz $K' \to K'_\infty, KK'' \to 0, K^2K''' \to 0$ and the ratio $(K^2K'''/KK'')_\infty$ is finite[7] for both the EOS under study.

We make use of these equations to calculate the values of γ, q and $\boldsymbol{\lambda}$ at different values of compressions. The fundamental relationship between thermal pressure and thermal energy and therefore it is applicable for metals.

RESULTS AND DISCUSSION

Values of input parameters used in the present calculations are given in Table 1 (Rai *et al*., 2010 and Karbasi *et al*., 2011).

Table 1. Values of input for different metals at room temperature and zero pressure (Rai *et al*., 2010 and Karbasi *et al*., 2011)

Metals	Pt	Fe	V	Nb
K_0	276.1	171.11	162.0	168.0
K_0'	5.30	7.79	3.50	3.30
K_∞'	3.18	4.67	2.10	1.98
K_0K_0''	-11.24	-24.27	-4.90	-4.36

Table 2. Values of pressure P, bulk modulus K, pressure derivatives of bulk modulus K', KK'' and K^2K''' for the different metals calculated from (a) Stacey EOS, (b) Kushwah logarithmic EOS

Metals	V/V_0	P		K		K'		KK''		K^2K'''	
		(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
	1.00	0.00	0.00	277.00	277.00	5.61	5.61	-12.59	-12.59	197.75	191.07
	0.95	16.39	16.38	364.20	364.14	5.09	5.09	-8.00	-8.04	102.99	105.15
	0.90	38.95	38.96	474.71	474.66	4.73	4.73	-5.49	-5.41	60.67	62.10
	0.85	70.00	70.03	617.29	617.36	4.47	4.47	-3.94	-3.79	38.64	38.76
	0.80	112.90	112.93	804.31	804.80	4.26	4.28	-2.92	-2.75	25.93	25.31
Pt	0.75	172.56	172.64	1053.5	1055.4	4.10	4.12	-2.21	-2.05	18.06	17.16
	0.70	256.47	256.75	1391.6	1396.9	3.96	4.00	-1.69	-1.56	12.91	12.01
	0.65	376.06	377.10	1859.0	1872.2	3.85	3.90	-1.31	-1.20	9.40	8.63
	0.60	550.11	552.79	2521.8	2549.9	3.76	3.81	-1.01	-0.94	6.92	6.32
	0.55	809.40	815.64	3487.4	3543.2	3.68	3.74	-0.78	-0.74	5.12	4.70
	0.50	1207.3	1221.0	4940.9	5048.0	3.62	3.68	-0.60	-0.58	3.79	3.53
	1.00	0.00	0.00	183.00	183.00	5.28	5.28	-11.15	-11.15	164.86	161.68
	0.95	10.73	10.73	236.90	236.90	4.82	4.82	-7.26	-7.24	88.81	90.75
	0.90	25.31	25.31	304.54	304.56	4.49	4.50	-5.06	-4.93	53.42	54.36
	0.85	45.10	45.11	390.77	390.98	4.24	4.26	-3.68	-3.49	34.52	34.30
	0.80	72.06	72.09	502.38	503.23	4.05	4.08	-2.75	-2.55	23.43	22.60
Fe	0.75	109.05	109.18	649.15	651.55	3.90	3.93	-2.10	-1.92	16.47	15.45
	0.70	160.35	160.75	845.53	851.18	3.77	3.82	-1.62	-1.47	11.86	10.90
	0.65	232.53	233.56	1113.4	1125.3	3.66	3.72	-1.26	-1.15	8.70	7.89
	0.60	335.97	338.37	1487.4	1510.7	3.57	3.64	-0.98	-0.91	6.44	5.84
	0.55	487.59	492.84	2023.1	2067.1	3.50	3.57	-0.77	-0.72	4.80	4.38
	0.50	716.19	727.27	2814.9	2896.2	3.43	3.51	-0.60	-0.57	3.58	3.32
	1.00	0.00	0.00	162.00	162.00	3.50	3.50	-4.90	-4.90	48.02	48.74
	0.95	9.07	9.08	192.70	192.73	3.28	3.28	-3.65	-3.60	31.30	31.96
	0.90	20.47	20.47	229.07	229.09	3.12	3.12	-2.79	-2.72	21.44	21.68
	0.85	34.76	34.70	272.45	272.63	2.98	2.98	-2.19	-2.10	15.26	15.14
	0.80	52.83	52.88	342.96	325.43	2.87	2.87	-1.74	-1.65	11.16	10.85
V	0.75	75.84	75.92	389.31	390.32	2.77	2.77	-1.40	-1.32	8.33	7.95
	0.70	105.37	105.56	469.17	471.18	2.69	2.69	-1.14	-1.06	6.32	5.94
	0.65	143.77	144.17	569.85	573.55	2.62	2.62	-0.93	-0.87	4.85	4.52
	0.60	197.44	195.19	699.07	705.44	2.56	2.56	-0.76	-0.72	3.75	3.48
	0.55	262.31	263.87	867.88	878.85	2.50	2.50	-0.62	-0.59	2.91	2.71
	0.50	355.46	358.36	1094.3	1112.4	2.45	2.45	-0.51	-0.49	2.27	2.13
	1.00	0.00	0.00	168.80	168.80	3.30	3.30	-4.36	-4.36	40.25	40.18
	0.95	9.43	9.42	198.93	198.89	3.11	3.11	-3.29	-3.28	26.81	27.22
	0.90	21.11	21.11	234.22	234.24	2.95	2.95	-2.55	-2.52	18.69	18.96
	0.85	35.69	35.67	276.21	276.22	2.82	2.82	-2.02	-1.97	13.46	13.52
	0.80	53.89	53.92	326.47	326.70	2.72	2.72	-1.62	-1.56	9.95	9.85
Nb	0.75	76.88	76.94	387.62	388.15	2.63	2.63	-1.32	-1.26	7.50	7.30
	0.70	106.17	106.27	462.92	463.99	2.55	2.55	-1.08	-1.02	5.73	5.50
	0.65	143.87	144.08	556.97	558.99	2.48	2.48	-0.88	-0.84	4.42	4.21
	0.60	193.08	193.53	676.41	680.04	2.42	2.42	-0.73	-0.69	3.44	3.25
	0.55	258.46	259.33	831.12	837.34	2.37	2.37	-0.60	-0.57	2.69	2.53
	0.50	347.10	348.77	1036.1	1046.5	2.32	2.32	-0.49	-0.47	2.10	1.99

Table 2. Values of Grüneisen parameter (γ) and higher order volume derivatives of the Grüneisen parameter (q and λ) for the different metals calculated from (a) Stacey EOS, (b) Kushwah logarithmic EOS

Metals	V/V_0	γ		q		λ	
		(a)	(b)	(a)	(b)	(a)	(b)
	1.00	2.63	2.63	2.38	2.38	7.72	7.19
	0.95	2.37	2.37	1.67	1.68	6.10	6.30
	0.90	2.20	2.20	1.24	1.22	5.08	5.52
	0.85	2.07	2.07	0.95	0.91	4.38	4.83
	0.80	1.96	1.97	0.74	0.69	3.88	4.24
Pt	0.75	1.88	1.89	0.58	0.54	3.49	3.73
	0.70	1.82	1.83	0.46	0.42	3.20	3.30
	0.65	1.76	1.78	0.37	0.33	2.96	2.95
	0.60	1.72	1.74	0.29	0.27	2.77	2.66
	0.55	1.68	1.71	0.23	0.21	2.62	2.43
	0.50	1.64	1.67	0.18	0.17	2.49	2.23
	1.00	3.06	3.06	2.56	2.56	12.22	8.38
	0.95	2.77	2.75	1.49	1.70	9.20	7.50
	0.90	2.60	2.55	0.95	1.16	7.52	6.74
	0.85	2.48	2.41	0.64	0.80	6.43	6.06
	0.80	2.40	2.31	0.44	0.57	5.66	5.46
Fe	0.75	2.35	2.24	0.31	0.41	5.08	4.92
	0.70	2.30	2.19	0.23	0.29	4.63	4.47
	0.65	2.27	2.15	0.16	0.21	4.26	4.12
	0.60	2.25	2.12	0.12	0.16	3.96	3.89
	0.55	2.23	2.09	0.08	0.11	3.71	3.80
	0.50	2.21	2.07	0.06	0.08	3.50	3.91
	1.00	1.39	1.39	1.32	1.32	5.12	5.32
	0.95	1.30	1.30	1.04	1.02	4.40	4.83
	0.90	1.24	1.24	0.83	0.80	3.86	4.35
	0.85	1.19	1.19	0.68	0.63	3.45	3.89
	0.80	1.15	1.15	0.55	0.50	3.11	3.45
V	0.75	1.11	1.12	0.46	0.41	2.84	3.05
	0.70	1.08	1.09	0.38	0.34	2.61	2.69
	0.65	1.05	1.07	0.31	0.28	2.42	2.37
	0.60	1.03	1.05	0.26	0.23	2.25	2.10
	0.55	1.01	1.03	0.22	0.20	2.10	1.87
	0.50	0.99	1.01	0.18	0.17	1.97	1.68
	1.00	1.54	1.54	1.53	1.53	4.42	4.40
	0.95	1.43	1.43	1.24	1.24	3.81	3.96
	0.90	1.35	1.35	1.03	1.01	3.35	3.56
	0.85	1.28	1.28	0.86	0.83	2.99	3.20
	0.80	1.22	1.22	0.72	0.69	2.71	2.88
Nb	0.75	1.17	1.17	0.61	0.58	2.48	2.60
	0.70	1.12	1.13	0.52	0.49	2.28	2.35
	0.65	1.08	1.09	0.44	0.42	2.12	2.14
	0.60	1.05	1.06	0.37	0.35	1.98	1.96
	0.55	1.02	1.03	0.32	0.30	1.86	1.80
	0.50	0.99	1.00	0.27	0.25	1.75	1.66

Conclusion

The results for metals Pt, Fe, V and Nb for the calculation of Grüneisen parameter γ and its volume derivatives (q and λ) are identical from both the equations.

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