THE STUDY OF GRÜNEISEN PARAMETER OF METALS USING EQUATIONS OF STATE

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In the present study, 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 Ag, Cu and Au at different values of compression from (0.8 to 1.0).

KEYWORDS: Equation of State, Grüneisen parameter, Pressure.

INTRODUCTION

Studies on equation of state (EOS) are of central importance for predicting thermo elastic properties of materials at high pressures [1-3]. The Grüneisen parameter (γ) provides a useful link between thermal and elastic properties [4-6]. The Grüneisen parameter γ and its volume derivatives q and λ can be determined with help of pressure derivatives of bulk modulus [7, 8] using the free volume theory. In the present study we determine the Grüneisen parameter γ and its volume derivatives q and λ for metals silver, copper and gold at different values of compression down to V/V_0 (0.8 to 1.0).

We have used the Stacey reciprocal K-primed [10] and Kushwah generalized logarithmic EOS [11]. These EOS have been found to satisfy various thermodynamic constraints for material. The results have been found to good agreement with the stacey EOS [10, 12]. The free volume theory has been applied successfully by Holzapfel *et al*. [13] 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.

THEORY

The most important parameters providing connection between thermal and elastic properties is the Grüneisen parameter [1]

$$\gamma = \frac{\alpha K_T}{\rho C_V} = \frac{\alpha K_S}{\rho C_P} \quad \ldots (1)$$

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 [3, 7]

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

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

According to the generalized free volume theory [2, 9] we have the following expression for the Grüneisen parameter

$$\gamma = \frac{(1/2)K' - (1/6) - (f/3)(1-(1/3)(P/K))}{1-(2/3)f(P/K)} \quad \ldots (4)$$

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

$$\varepsilon = \frac{f(K - K'P)}{(3K - 2fP)} \quad \ldots (5)$$

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

$$q\gamma = -\frac{KK''}{2} + K\frac{d\varepsilon}{dP} \quad \ldots (6)$$

and

$$\gamma q(q+\lambda) = \frac{K'KK''}{2} + \frac{K^2K'''}{2}$$

$$-KK'\frac{d\varepsilon}{dP} - K^2\frac{d^2\varepsilon}{dP^2} \quad \ldots (7)$$

where the pressure derivatives of ε obtained from eq. [5] as follows

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

and

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

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

We make use of these equations to calculate the values of γ, q and $\boldsymbol{\lambda}$ at different values of compressions.

Result and discussion

Values of input parameters used in the present calculations are given in Table 1 [13, 14, 15].

Table 1 : Values of input for different metals at room temperature and zero pressure [13, 14, 15]

Metals	**Ag**	**Cu**	**Au**
K_0	99.65	133.4	166.7
K_0'	6.11	5.37	6.00
K_∞'	3.67	3.22	3.60
K_0K_0''	– 14.93	– 11.53	–14.40

Table 2 : Values of Grüneisen parameter (γ) and higher order volume derivatives of the Grüneisen parameter (q and $\boldsymbol{\lambda}$) for the different metals calculated from (*a*) Stacey reciprocal *K*-primed EOS and (*b*) Kushwah logarithmic EOS

Metals	V/V_0	γ		q		$\boldsymbol{\lambda}$	
		(a)	**(b)**	**(a)**	**(b)**	**(a)**	**(b)**
	1.00	1.64	1.64	1.49	1.49	7.72	7.53
	0.98	1.59	1.59	1.28	1.29	7.57	7.00
	0.96	1.55	1.55	1.09	1.12	7.42	6.56
	0.94	1.52	1.52	0.94	0.98	7.26	6.18
	0.92	1.49	1.49	0.80	0.86	7.08	5.85
Ag	0.90	1.47	1.46	0.69	0.76	6.89	5.56
	088	1.45	1.44	0.59	0.67	6.68	5.31
	0.86	1.43	1.42	0.51	0.59	6.47	5.09
	0.84	1.41	1.40	0.43	0.53	6.23	4.89
	0.82	1.40	1.38	0.37	0.47	5.98	4.70
	0.80	1.39	1.37	0.32	0.42	5.71	4.54

Metals	V/V_0	γ		q		λ	
		(a)	**(b)**	**(a)**	**(b)**	**(a)**	**(b)**
	1.00	1.97	1.97	1.74	1.74	8.07	8.66
	0.98	1.91	1.91	1.48	1.47	7.90	7.94
	0.96	1.85	1.85	1.26	1.25	7.72	7.35
	0.94	1.81	1.81	1.07	1.08	7.54	6.86
	0.92	1.77	1.77	0.91	0.93	7.35	6.45
Cu	0.90	1.74	1.74	0.78	0.81	7.15	6.09
	0.88	1.71	1.71	0.66	0.71	6.94	5.78
	0.86	1.68	1.68	0.56	0.62	6.71	5.51
	0.84	1.66	1.66	0.48	0.55	6.47	5.27
	0.82	1.65	1.64	0.41	0.48	6.22	5.05
	0.80	1.63	1.62	0.35	0.43	5.96	4.85

Metals	V/V_0	γ		q		λ	
		(a)	**(b)**	**(a)**	**(b)**	**(a)**	**(b)**
	1.00	2.36	2.36	2.04	2.04	7.98	9.24
	0.98	2.27	2.27	1.74	1.71	7.72	8.34
	0.96	2.20	2.20	1.48	1.45	7.46	7.62
	0.94	2.13	2.14	1.27	1.24	7.20	7.03
	0.92	2.08	2.09	1.09	1.07	6.95	6.53
Au	0.90	2.03	2.04	0.94	0.93	6.69	6.11
	0.88	1.99	2.00	0.81	0.81	6.43	5.75
	0.86	1.96	1.97	0.70	0.72	6.17	5.43
	0.84	1.93	1.93	0.61	0.63	5.91	5.15
	0.82	1.90	1.91	0.53	0.56	5.64	4.90
	0.80	1.88	1.88	0.46	0.50	5.38	4.68

Conclusion

The results for metals Ag, Cu and Au for the calculation of Grüneisen parameter γ and its volume derivatives (q and λ) are identical from both the equations.

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