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Brief report: Volume dependence of Grüneisen parameter for solids under extreme compression

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Abstract. The Nie expression is amended in such a way that the expression follows the infinite pressure behaviour, i.e., $P \to \infty$ or $V \to 0$. A new empirical relationship is developed to predict the values of volume dependence of Grüneisen parameter. NaCl and ε-Fe have been employed to test the suitability of the expression. The results obtained reveal that the relationship is reliable as there is a good agreement between the calculated and the experimental data.

Keywords. Grüneisen parameter; second Grüneisen parameter; NaCl.

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1. Introduction

Grüneisen parameter (γ) is an important parameter for studying thermal and elastic properties of solids. It is used to explain anharmonic properties of solids in condensed matter physics and geophysics. Grüneisen parameter is useful for predicting the Debye temperature (θ_D) for solids and geophysical minerals. The knowledge of Grüneisen parameter is also required for investigating the melting curves from Lindemann–Gilvarry criterion [1,2]. Grüneisen parameter has both microscopic and macroscopic definitions. Lattice harmonicity leads to a volume dependence of phonon frequencies (ω_i), that is described by the mode Grüneisen parameter [3];

$$\gamma_i = -\left(\frac{\mathrm{d}\ln\omega_i}{\mathrm{d}\ln V}\right)_{\mathrm{T}}. \tag{1}$$

The mechanical Grüneisen parameter is defined as the average of γ_i over the first Brillouin zone, $\gamma_m = \langle\gamma_i\rangle$. When all the γ_i are equal, it can be shown [4] that $\gamma_m = \gamma_i$ which coincides with the thermodynamic Grüneisen parameter [5]

$$\gamma_{\mathrm{th}} = \frac{\alpha K_{\mathrm{T}} V}{C_{\mathrm{V}}}, \tag{2}$$

where α, K_T, V and C_V are respectively the volume thermal expansivity, isothermal bulk modulus, volume and heat capacity at constant volume.

One common experimental research of Grüneisen parameter in its macroscopic definition has been done by Birch [6] based on experimental measurement of thermodynamic properties at high temperatures and high pressures. The experimental determination of the Grüneisen parameter defined in the microscopic definition is extremely difficult, as it requires a detailed knowledge of the phonon dispersion spectrum of a solid [7]. There is a long history of attempts to study Grüneisen parameter [8] by the following relationship:

$$\gamma = \frac{(1/2)K'_{\mathrm{T}} - (1/6) - (f/3)\,(1 - (P/3K_{\mathrm{T}}))}{1 - (2/3)f(P/K_{\mathrm{T}})}, \tag{3}$$

where P, K_T and K'_T are respectively the pressure, isothermal bulk modulus and the first-order pressure derivative of isothermal bulk modulus, and f is the parameter which takes different values for different derivations of γ, based on different approximations. Hence $f = 0$ for Slater's formula [9], $f = 1$ for Dugdale and MacDonald formula [10], $f = 2$ for free volume formula [11] and $f = 2.35$ in molecular dynamical calculation by Barton and Stacey [12].

At $P = 0$, eq. (3) becomes

$$\gamma_0 = \frac{1}{2}K_0' - \frac{1}{6} - \frac{f}{3}. \quad (4)$$

The value of f [13] can be calculated using eq. (4). Many expressions [14–24] have been made for estimating the volume or pressure dependence of Grüneisen parameter.

The second-order Grüneisen parameter (q) may be expressed as [25]

$$q = q_0\left(\frac{V}{V_0}\right)^{\lambda}, \quad (5)$$

where q_0 is the second Grüneisen parameter at zero pressure and λ is a material-dependent fitting parameter. q is defined as

$$q = \left(\frac{\mathrm{d}\ln\gamma}{\mathrm{d}\ln V}\right)_{\mathrm{T}}. \quad (6)$$

One can get subsequent expression for volume dependence of the Grüneisen parameter as given below:

$$\gamma = \gamma_0 \exp\left[\left(\frac{q_0}{\lambda}\right)\left\{\left(\frac{V}{V_0}\right)^{\lambda} - 1\right\}\right], \quad (7)$$

where all parameters have their usual meaning. Similar expression has been used by Hui and Bao [17] to study the volume dependence of Grüneisen parameter for lithium, sodium and potassium at 298 K. In the present paper, a new simple and straightforward relationship for volume dependence of Grüneisen parameter is derived. This expression is applied on NaCl and ε-Fe for which experimental data are available.

2. Method of analysis

Peng *et al* [26] have shown that eq. (7) gives better results than others [15,18]. Srivastava and Sinha [23] also preferred eq. (7) to formulate the expression for investigating the values of volume dependence of Grüneisen parameter. At infinite pressure i.e., $P \to \infty$ or $V \to 0$, eq. (7) takes the form

$$\gamma_\infty = \gamma_0 \exp\left(-\frac{q_0}{\lambda}\right). \quad (8)$$

Applying $P \to \infty$ or $V \to 0$ in eq. (3), we get

$$\gamma_\infty = \frac{(1/2)K_\infty' - (1/6) - (f/3)\left(1 - (1/3)(P/K_{\mathrm{T}})_\infty\right)}{1 - (2/3)f\,(P/K_{\mathrm{T}})_\infty}, \quad (9)$$

where $(P/K_{\mathrm{T}})_\infty \to 0$ [13,27], $K_\infty' \to +$ve and finite [13,27,28], and $f = 0$ [9]. Now eq. (9) becomes

$$\gamma_\infty = \frac{1}{2}K_\infty' - \frac{1}{6}, \quad (10)$$

where K_∞', the first-order pressure derivative of isothermal bulk modulus (K_{T}) at infinite pressure limit is an important parameter. This parameter remains constant under different temperatures for a material of interest.

After rearranging eq. (8), we get

$$\frac{q_0}{\lambda} = \ln\left(\frac{\gamma_0}{\gamma_\infty}\right). \quad (11)$$

Following Thomas Fermi model, i.e., $K_\infty' = 5/3$ [29–32], we find $\gamma_\infty = 2/3$ from eq. (7) which is consistent with earlier works [33–35]

By using eqs (7) and (11), we get

$$\gamma = \gamma_0 \exp\left[\ln(1.5\gamma_0)\left\{\left(\frac{V}{V_0}\right)^{\lambda} - 1\right\}\right]. \quad (12)$$

It is necessary to note down here that eq. (12) satisfies the high-pressure thermodynamics limit, i.e., $P \to \infty$ or $V \to 0$. Equation (12) gives $\gamma_\infty = 2/3$ [33–35] at $P \to \infty$ or $V \to 0$.

3. Results and discussions

The modified expression, eq. (12), is established for predicting the values of volume dependence of Grüneisen parameter along an isotherm at extreme compression. The reliability of eq. (12) has been tested on NaCl and ε-Fe. The values of the fitted parameter λ are found to be 1.413 and 0.81 for NaCl and ε-Fe respectively, by using the experimental values of volume dependence of Grüneisen parameter in eq. (12). The values of γ_0 for NaCl and ε-Fe are 1.6275 [36] and 1.71 [37] respectively. The results obtained using eq. (12) are shown in figures 1 and 2, along with available experimental data [6,36] for comparison. It is evident from the figures that results obtained from eq. (12) throughout the compression region show consistency with available data [6,36]. In the given range of volume, the experimental data points appear to be approximately linear, whereas the relation (eq. (12)) is nonlinear. Within a narrow range, even a highly nonlinear relation may behave as roughly linear. Therefore, instead of looking at the actual values, one must look at the curvature of the theoretical plot to assess the suitability of an analytical model. It can be noted from figures 1 and 2 that the results obtained from eq. (12) and ref. [17] are the same. Equations (7) and (12) are

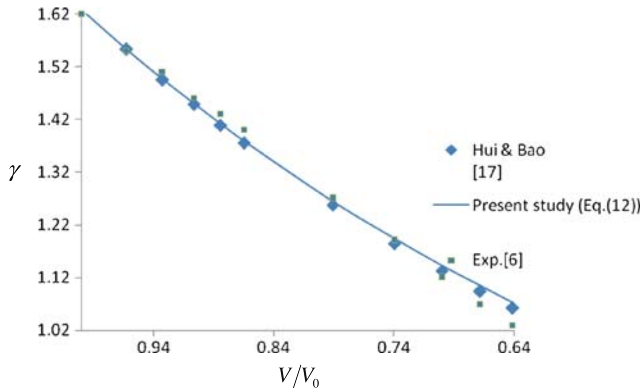

Figure 1. Volume dependence of Grüneisen parameter predicted by eq. (12) along with experimental data and data from Hui and Bao [17] for NaCl.

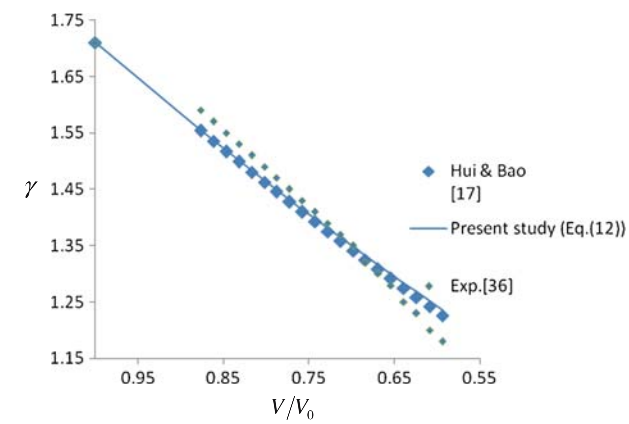

Figure 2. Volume dependence of Grüneisen parameter predicted by eq. (12) along with experimental data and data from Hui and Bao [17] for ε-Fe.

similar except that in eq. (12), q_0 is replaced using eq. (11). In effect, the numbers of fitting parameters have been reduced to one, instead of two but the important thing is that eq. (12) satisfies the infinite pressure behaviour limit. However, eq. (7) does not hold this limit.

The value of fitted parameter λ discloses a method to compute the value of q_0 with the help of eq. (11); we get $q_0 = 1.26$, in case of NaCl. Cui and Yu [21] and Xing *et al* [38] have estimated $q_0 = 1.5$ and 1.1 respectively. Many researchers [22,23,39] suggested $q_0 = 1.2$ for NaCl. The value $q_0 = 1.26$ for NaCl obtained in the present study is very near to the value obtained by earlier researchers [21–23,38,39]. We found $q_0 = 0.76$ for ε-Fe which is consistent with the available data [19,23,40]. This analysis also validates our relationship (eq. (12)).

4. Conclusions

In the present paper, we have amended the Nie [16] expression in such a way that it may satisfy the thermodynamic limit, i.e., $P \rightarrow \infty$ or $V \rightarrow 0$. The empirically modified relationship is applied to various materials to judge the suitability. A close agreement between the theory and the experiment reveals the validity of the present approach.

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