# Theoretical prediction of validity of isothermal EOS for calculation of Grüneisen Parameter for bcc elements

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## Abstract

The Grüneisen parameter (γ) is of considerable importance to Earth scientists because it sets limitations on the thermoelastic properties of the lower mantle and core. However, there are several formulations of the Grüneisen parameter in frequent use which not only give different values for γ at ambient pressure but also predict a varying dependence of γ as a function of compression. The Grüneisen parameter is directly related to the equation of state (EOS), yet it is often the case that both the form of γ and the EOS are chosen independently of each other and somewhat arbitrarily. In this paper we have assessed some of the more common definitions of the Grüneisen parameter and the EOS, and have applied them to a test the validity of EOS for eight different bcc elements.

**Key Words**: Grüneisen parameter ,EOS, Acoustic gamma, Bulk modulus

## Introduction

The Grüneisen parameter has considerable appeal to geophysicists because it is an approximately constant, dimensionless parameter that varies slowly as a function of pressure and temperature. It has both a microscopic and macroscopic definition, the former relating it to the vibrational frequencies of atoms in a material, and the latter relating it to familiar thermodynamic properties such as heat capacity and thermal expansion. Unfortunately, the experimental determination of Grüneisen parameter (γ), defined in either way, is extremely difficult; the macroscopic definition requires a detailed knowledge of the phonon dispersion spectrum of the material, whereas the microscopic definition requires experimental measurements of thermodynamic properties at high pressure and temperature. As a result of the difficulty associated with obtaining experimentally an accurate value for Grüneisen parameter (γ), [a number of more approximate expressions have been suggested by Poirire [1]] many of these relate Grüneisen parameter (γ) at atmospheric pressure (P=0) to the first derivative of the bulk modulus with respect to pressure $K_T^{'}$ via γ = (1/2)$K_T^{'}$–X, where X is constant. These relations may be expanded to take into account the variation of Grüneisen parameter (γ) with pressure. In these more general cases, Grüneisen parameter γ(P) is a function of the equation of state. Despite the intrinsic relationship between

Grüneisen parameter (γ) and equation of state [2], it is frequently the case that the choice of the functional form of both the Grüneisen parameter and the equation of state to which it should be related are made independently of each other, and somewhat arbitrarily; this has resulted in a literature in which there is a wide range of value of Grüneisen parameter (γ) for many geologically relevant materials. It is therefore, important to investigate more carefully how the value of Grüneisen parameter (γ) and its compressional behaviour are affected by:

(1) the choice of the formulation of Grüneisen parameter (γ)
(2) the use of different equation of state.

Temperature, as found in the P-V-T equations involving solids, is nearly always associated with the important anharmonic parameter called the Grüneisen parameter Grüneisen parameter (γ). This parameter has been approximated in a variety of ways, since in its most general sense, according to solid state physics, it is a tensor quantity arising from definition of how the various frequencies of vibration in the lattice vary with volume. In applying this generalised concept to P-V-T relationship (which are necessarily scalar), some particular physical assumption has to be invoked in order to produce an average Grüneisen parameter (γ) ; that is some average derivative of frequency with volume must be used in place of general definitions.

We shall firstly review the various formulations of Grüneisen parameter (γ), starting how they may be they be obtained directly from the equation of state. In the present work the Grüneisen parameter has been estimated at different compression for 8 elements viz. Ba, Er, Fe, La, Mo, K, Rb and Na using three phenomenological isothermal equations of state.

**The Grüneisen Parameter**

The Grüneisen ratio (γ) [3,4] is a very important thermodynamic parameter used to help quantitatively the relationship between the thermal and elastic properties of solid. Sometimes Grüneisen parameter (γ) is called the thermal Grüneisen parameter. The Grüneisen ratio can be considered as the measure of change of the pressure resulting from the increase of energy density at constant volume V. It is dimensionless, as ΔP and Δu/V have the same units. A convenient form is $\gamma = \left(\frac{\partial P}{\partial u}\right)_v V$ (1)

If the change in pressure were exactly proportional to change in energy density, Grüneisen parameter (γ) would be independent of P and T, and experiments show this to be nearly correct if one considers the case for the variation of Grüneisen parameter (γ) with T at constant V. In fact the proportionality constant usually lies between 1 and 2.

Now from equation (1) we have

$$\left(\frac{\partial P}{\partial u}\right)_V = \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial u}{\partial T}\right)_V} \quad (2)$$

But $$\left(\frac{\partial u}{\partial T}\right)_V = C_V$$

where $C_V$ is specific heat for unit mass at constant volume, and

$$\left(\frac{\partial P}{\partial T}\right)_V = \alpha K_T$$

where α is compressibility

Thus, equation (2) reduces to

$$\left(\frac{\partial P}{\partial u}\right)_V = \frac{\alpha K_T}{C_V} \tag{3}$$

Using this in equation (1) we have

$$\gamma = \frac{\alpha K_T V}{C_V} \tag{4}$$

Thus Grüneisen parameter (γ) given by equation (4) is composed of individual measurable physical properties, each of which varies significantly with temperature, but the ratio of these properties as given by the equation (4) does not vary greatly with temperature, and some time not at all.

The microscopic definition of Grüneisen parameter [5] is written in terms the volume dependence of the $i^{th}$ mode of vibration of lattice ($\omega_i$) and is given by

$$\gamma_i = -\frac{\partial \ln \omega_i}{\partial \ln V} \tag{5}$$

However, evaluation of all $\gamma_i$ throughout the Brillouin Zone is impossible without some lattice dynamical model or high pressure inelastic neutron scattering data. It can be shown [6] that the sum of all $\gamma_i$ throughout the first Brillouin Zone leads to a macroscopic or thermodynamic definition of Grüneisen parameter (γ) which may be written as

$$\gamma_{th} = \left(\frac{\alpha V K_T}{C_V}\right) \tag{6}$$

Where α is the thermal expansion coefficient, V the volume, $K_T$ the isothermal bulk modulus and $C_V$ is the heat capacity at constant volume. Evaluation of $\gamma_{th}$ is also very difficult, however, because it requires experimental measurements of α, $K_{T,}$ etc. at extreme condition of pressure and temperature which are not readily attainable.

Integrating equation (6) with respect to temperature at constant volume leads to the Mie-Grüneisen Expression [1] for Grüneisen parameter (γ)

$$\gamma = \frac{P_{th}V}{E_{th}} \tag{7}$$

Where $P_{th}$ is the thermal pressure and $E_{th}$ the thermal energy. This too is difficult to determine because the thermal energy is not readily obtained experimentally. However, it is possible, in principle, to obtain $P_{th}$ and $E_{th}$ from ab initio free energy calculations, which therefore give us opportunity of using this approach to obtain the true thermodynamic Grüneisen parameter (γ) of a material.

Barron [6] showed that in general for the high temperature approximation the Grüneisen parameter can be written as

$$\gamma = \gamma^{ht} = \left(\frac{1}{3pN}\right)\sum_{j=1}^{3pN}\gamma_j \tag{8}$$

A further approximation is made by ignoring all optical modes of the crystal and also ignoring all acoustic modes except those at low wave number in the summation of equation (8). Thus, the summation up to 3pN is replaced by a summation up to 3 because most of the energy is in the high modes, this approximation appears weak but equation (8) is an average Grüneisen parameter (γ), and the approximation implies that the average of the three acoustic modes is equal to the average of all modes. Barron [6,7] showed that for the acoustic modes

$$\gamma_i = \frac{1}{3} - \frac{V}{\upsilon_i}\left(\frac{\partial \upsilon_i}{\partial V}\right)_T \tag{9}$$

$$= \frac{1}{3} + \frac{K_T}{\upsilon_i}\left(\frac{\partial \upsilon_i}{\partial P}\right)_T \tag{10}$$

Where (i=1, 2, 3) and $\upsilon_i$ is sound velocity. An alternative to equation (8) is

$$\gamma_i = -\frac{1}{6} + \frac{1}{2}\frac{K_T}{M_i}\left(\frac{\partial M_i}{\partial P}\right)_T \tag{11}$$

Where $M_i$ is the elastic modulus associated with $\upsilon_i$ found in equation (9).

The high temperature approximation (8) for a single crystal needs to account for the fact that $\gamma_i$ varies with direction. Barron [6] showed that one must use

$$\gamma^{ht} = \frac{1}{12\pi}\int\left(\sum_{i=1}^{3}\gamma_i\right)d\Omega \tag{12}$$

The reduction of (12) to materials isotropic to acoustic waves is obvious because there are only two sound velocities and two values of the mode gamma $\gamma_i$ , the isotropic γ's are

$$\gamma_s = -\frac{1}{6} + \frac{1}{2}\frac{K_T}{G}\left(\frac{\partial G}{\partial P}\right)_T \tag{13}$$

And $$\gamma_P = -\frac{1}{6} + \frac{1}{2}\frac{K_T}{\rho v_P^2}\left(\frac{\partial \rho v_p^2}{\partial P}\right)_T \tag{14}$$

where G is isotropic shear modulus

The acoustic approximation to the Grüneisen ratio called $\gamma_{ac}$, is thus the average of the P wave mode $\gamma_P$ and two shear wave modes $\gamma_s$

$$\gamma_{ac} = \frac{1}{3}(\gamma_P + 2\gamma_s) \tag{15}$$

Equation (15) can be applied immediately to isotropic polycrystalline materials, however most application of equation (15) to mineral are made by finding the equivalent isotropic elastic constants $K_s$ and G, of the single crystal at each pressure and the average associated pressure derivatives of the $K_s$ and G values [8], because both $\gamma_s$ and $\gamma_p$ can be expressed in terms of different sets of elastic constant pressure derivatives, alternate form of (13) can be generated. One form uses the pressure derivative of the bulk modulus K and the Poisson ratio υ, so that

$$\gamma_{ac} = \frac{1}{2}\left(\frac{dK}{dP}\right) - \frac{1}{6} - \left(\frac{(4-5\upsilon)}{(1+\upsilon)(1-\upsilon)(1-2\upsilon)}\right)\left(\frac{K_T}{3}\right)\left(\frac{d\upsilon}{dP}\right) \tag{16}$$

If dυ/dP is assumed to be zero, equation (16) reduces to the expression of Grüneisen parameter (γ) known as Slater gamma ($\gamma_{sl}$) [9] which is traditionally derived from entirely different premises, we then find that

$$\gamma_{sl} = \left(\frac{1}{2}\right)\left(\frac{dK}{dP}\right) - \frac{1}{6} \tag{17}$$

The free volume expression for Grüneisen parameter (γ) was derived by Vashchenko and Zubarev [10] & Irvine and Stacey [2] followed by the path suggested by Brillouin [11], who showed that the thermal pressure may be considered as that required to keep the volume constant as the temperature raised , they expended the "mutual forces between the atoms at separation r" in a series expansion around $r_0$ to quadratic terms and found the pressure necessary to keep ΔV zero at given T, and solved for Grüneisen parameter (γ)

$$\gamma_{VZ} = \frac{\left(\frac{1}{2}\right)K' - \frac{5}{6} + \frac{2}{9}\left(\frac{P}{K_T}\right)}{1 - \left(\frac{4}{3}\right)\left(\frac{P}{K_T}\right)} \tag{18}$$

Where the subscript refers to Vashchenko's and Zubarev's

Again Stacey assumed that the correlation of motions along a bond was the same with respect to dilation as that of those transverse to the bond. Thus, Borton and Stacey [12], find correlation for Grüneisen parameter (γ) leading to

$$\gamma_{ba-s} = \frac{\left(\frac{1}{2}\right)K' - \frac{1}{6} - \frac{f}{3}\left[1 - \frac{1}{3}\left(\frac{P}{K_T}\right)\right]}{1 - \left(\frac{4}{3}\right)\left(\frac{P}{K_T}\right)} \tag{19}$$

Where f=2.35 not 2 as in equation (18)

At P=0, equation (19) reduces to

$$\gamma_{ba-s} = \frac{1}{2}K_0^{'} - 0.95 \tag{20}$$

An another approach for shock waves has been the use of Dugdale and MacDonald equation[13]

$$\gamma_{D-M} = -\frac{1}{3} - \frac{V}{2}\left(\frac{\partial\left(PV^{2/3}\right)}{\partial V}\right)_T^{-1}\left(\frac{\partial^2\left(PV^{2/3}\right)}{\partial V^2}\right)_T \tag{21}$$

at zero pressure above expression can be written as

$$\gamma_{D-M} = -\frac{1}{2} + \frac{1}{2}\left(\frac{\partial K_T}{\partial P}\right)_T \tag{22}$$

In there derivation Dugdale and MacDonald constructed a mode of a primitive cubic lattice composed of atoms connected by simple springs. They considered propagated along the springs which is really one dimensional propagation. Pastine [34] pointed out that this consists of assuming only longitudinal wave propagating along cubic axes with no transverse waves.

**Computation of Grüneisen parameter (γ) From Equation of State**

The three phenomenological forms of isothermal equation of state as derived from lattice potential theory [15] are as follows:

$$P = \frac{3K_0\left(\frac{V}{V_0}\right)^{-\frac{4}{3}}}{(3K_0^{'} - 5)}\left[\exp\left\{\left(\frac{3K_0^{'} - 5}{3}\right) \times \left(1 - \frac{V}{V_0}\right)\right\} - 1\right] \tag{23}$$

$$P = \frac{3K_0\left(\frac{V}{V_0}\right)^{-\frac{4}{3}}}{(3K_0^{'}-8)}\left[\left(1-\frac{1}{t}+\frac{2}{t^2}\right)(\exp(ty)-1)+y\left(1+y-\frac{2}{t}\right)\exp(ty)\right] \quad (24)$$

where y = (1-V/$V_0$) and t = ( $K_0^{'}$ -8/3)

$$P = 3K_0x^{-2}(1-x)\exp[\eta(1-x)] \quad (25)$$

where x=$(V/V_0)^{1/3}$ and η=(3/2)( $K_0^{'}$ -1)

V is the volume at pressure P and $V_0$ is the volume at zero pressure, $K_0$ and $K_0^{'}$ are the isothermal bulk modulus and its first pressure derivative at zero pressure respectively. Equation (23) is the Brennan-Stacey EOS derived, using the thermodynamic formulation for the Grüneisen parameter [16,17]. Equation (24) is the Shanker EOS derived using a modified exponential dependence for the short range force constant on volume [18]. Equation (25) is the Vinet EOS based on universal relationship between binding energy and interatomic separation for solids [19,20]. Expression for isothermal bulk modulus corresponding to equations (23), (24), and (25) obtained using the relationship $K_T$=-V$(dP/dV)_T$ are given as follows:

$$K_T = K_0\left(\frac{V}{V_0}\right)^{-\frac{1}{3}}\exp\left\{\left(K_0^{'}-\frac{5}{3}\right)\left(1-\frac{V}{V_0}\right)\right\}+\frac{4}{3}P \quad (26)$$

$$K_T = K_0\left(\frac{V}{V_0}\right)^{-\frac{4}{3}}\exp\left\{\left(K_0^{'}-\frac{8}{3}\right)\left(1-\frac{V}{V_0}\right)\right\}+\frac{4}{3}P \quad (27)$$

$$K_T = K_0x^{-2}[1+(\eta x+1)(1-x)]\exp\{\eta(1-x)\} \quad (28)$$

The corresponding expression for $K_T^{'}$ =($dK_T/dP$) obtained from equations (26), (27), and (28) are written as follows:

$$K_T^{'} = \left(1-\frac{4}{3}\frac{P}{K_T}\right)\left\{\left(K_0^{'}-\frac{5}{3}\right)\frac{V}{V_0}+\frac{5}{3}\right\}+\frac{16}{9}\frac{P}{K_T} \quad (29)$$

$$K_T^{'} = \left(1-\frac{4}{3}\frac{P}{K_T}\right)\left\{\left(K_0^{'}-\frac{8}{3}\right)\frac{V}{V_0}+\frac{8}{3}\right\}+\frac{16}{9}\frac{P}{K_T} \quad (30)$$

$$K_T^{'} = \frac{1}{3}\left[\frac{x(1-\eta)+2\eta x^2}{1+(\eta x+1)(1-x)}+\eta x+2\right] \quad (31)$$

Thus equations (23), (26), and (29) represent the Brennan Stacey EOS, equations (24), (27), and (30) represent the Shanker EOS and equations (25), (27), and (31), represent the Vinet EOS.

**Results and Discussion**

In the present work we have described three different forms of EOS; equations (23), (24), and (25). Equation (23) corresponds to Brennan-Stacey EOS, equation (24) corresponds to Shanker EOS and equation (25) corresponds to Vinet EOS. All the three EOS contains only two parameters $K_0$ and $K_0^{'}$ both at zero pressure. It has been the usual practice to adjust or to fit the parameters $K_0$ and $K_0^{'}$ in order to achieve the agreement with the experimental values. This procedure of fitting does not provides an useful insight for the physical EOS. In order to make a real test of EOS we have used experimental values of $K_0$ and $K_0^{'}$ for given elements. These values of $K_0$ and $K_0^{'}$ have been recommended by Anderson [21]. The values of pressure P for eight elements viz. Ba, Er, Fe, La, Mo, K, Rb & Na were computed for given increments of $V/V_0$ by using equation (23), (24) and (25). The value of input parameter, $K_0$ and $K_0^{'}$ are taken from literature [21, 22]. Using the value of pressure P computed from equations (23), (24) and (25) for eight elements, the values of first pressure derivative of bulk modulus ($K_T$) at constant temperature are computed from equations (26), (27) and (28). Substituting these values P and $K_T$, in equations (29), (30) and (31) the value of $K_T^{'}$ was obtained. Further substituting the values of P, $K_T$ and $K_T^{'}$, in equation (19) the value of $\gamma_{ba\text{-}s}$ were calculated. A graph is plotted between the Grüneisen parameter ($\gamma$) versus $V/V_0$, leads to the following generalization.

Table 1: Input value of Bulk modulus (K0) and its first pressure derivative ( ) for different elements at zero pressure

| S.No | Element | $K_0$ | $K_0^{'}$ |
|---|---|---|---|
| 22 | Lithium | 11.80 | 3.33 |
| 28 | Sodium | 6.20 | 3.50 |
| 26 | Potassium | 3.40 | 2.99 |
| 27 | Rubidium | 2.66 | 3.23 |
| 4 | Barium | 9.46 | 1.73 |
| 19 | Iron | 171.11 | 7.79 |
| 13 | Erbium | 44.91 | 3.54 |
| 23 | Molubdenum | 253.10 | 13.29 |

Table 2: Calculated values of pressure (P) , isothermal bulk modulus ( KT ), its first pressure derivative ( ),and Barton-Stacey Grüneisen parameter (γba-s) at different compressions (V/V0) for Lithium using (a) Brennan- Stacey EOS (b) Shanker EOS (c) Vinet EOS at T=T0=300K

| $V/V_0$ | P (a) | P (b) | P (c) | $K_T$ (a) | $K_T$ (b) | $K_T$ (c) | $K_T'$ (a) | $K_T'$ (b) | $K_T'$ (c) | $\gamma_{ba-s}$ (a) | $\gamma_{ba-s}$ (b) | $\gamma_{ba-s}$ (c) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.00 | 0.00 | 0.00 | 0.00 | 11.80 | 11.80 | 11.80 | 3.33 | 3.33 | 3.33 | 0.83 | 0.83 | 0.83 |
| 0.90 | 1.48 | 1.48 | 1.48 | 16.40 | 16.48 | 16.44 | 2.94 | 3.03 | 2.88 | 0.75 | 0.80 | 0.71 |
| 0.80 | 3.77 | 3.79 | 3.78 | 22.75 | 23.20 | 22.94 | 2.63 | 2.79 | 2.52 | 0.67 | 0.77 | 0.59 |
| 0.70 | 7.39 | 7.48 | 7.45 | 31.74 | 33.13 | 32.33 | 2.37 | 2.59 | 2.22 | 0.58 | 0.73 | 0.47 |
| 0.60 | 13.25 | 13.52 | 13.47 | 44.88 | 48.43 | 46.39 | 2.14 | 2.42 | 1.97 | 0.50 | 0.70 | 0.35 |
| 0.50 | 23.19 | 23.87 | 23.84 | 65.07 | 73.26 | 68.51 | 1.94 | 2.27 | 1.76 | 0.42 | 0.67 | 0.23 |
| 0.40 | 41.23 | 42.84 | 43.06 | 98.42 | 116.73 | 105.85 | 1.77 | 2.15 | 1.56 | 0.33 | 0.63 | 0.09 |
| 0.30 | 77.85 | 81.63 | 82.91 | 160.27 | 202.32 | 175.90 | 1.63 | 2.04 | 1.39 | 0.25 | 0.60 | -0.10 |
| 0.20 | 168.84 | 178.58 | 183.42 | 301.46 | 409.63 | 333.36 | 1.50 | 1.95 | 1.21 | 0.17 | 0.57 | -0.39 |

Table 3: Calculated values of pressure (P) , isothermal bulk modulus ( KT ), its first pressure derivative ( ), Barton Stacey Grüneisen parameter (γba-s) and different compressions (V/V0) for Sodium using (a) Brennan- Stacey EOS (b) Shanker EOS (c) Vinet EOS at T=T0=300K

| $V/V_0$ | P (a) | P (b) | P (c) | $K_T$ (a) | $K_T$ (b) | $K_T$ (c) | $K_T'$ (a) | $K_T'$ (b) | $K_T'$ (c) | $\gamma_{ba-s}$ (a) | $\gamma_{ba-s}$ (b) | $\gamma_{ba-s}$ (c) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.00 | 0.00 | 0.00 | 0.00 | 6.20 | 6.20 | 6.20 | 3.50 | 3.50 | 3.50 | 0.92 | 0.92 | 0.92 |
| 0.90 | 0.78 | 0.78 | 0.78 | 8.76 | 8.80 | 8.78 | 3.08 | 3.17 | 3.00 | 0.83 | 0.88 | 0.78 |
| 0.80 | 2.02 | 2.03 | 2.02 | 12.33 | 12.57 | 12.44 | 2.74 | 2.90 | 2.61 | 0.73 | 0.83 | 0.65 |
| 0.70 | 3.99 | 4.04 | 4.03 | 17.42 | 18.19 | 17.78 | 2.46 | 2.68 | 2.29 | 0.64 | 0.79 | 0.52 |
| 0.60 | 7.23 | 7.38 | 7.36 | 24.95 | 26.94 | 25.90 | 2.21 | 2.50 | 2.02 | 0.55 | 0.75 | 0.39 |
| 0.50 | 12.79 | 13.17 | 13.20 | 36.59 | 41.26 | 38.83 | 2.00 | 2.34 | 1.80 | 0.46 | 0.71 | 0.26 |
| 0.40 | 23.00 | 23.91 | 24.19 | 55.94 | 66.56 | 60.99 | 1.82 | 2.20 | 1.59 | 0.37 | 0.67 | 0.11 |
| 0.30 | 43.93 | 46.10 | 47.39 | 91.99 | 116.79 | 103.25 | 1.65 | 2.08 | 1.41 | 0.28 | 0.63 | -0.07 |
| 0.20 | 96.42 | 102.10 | 107.14 | 174.52 | 239.38 | 200.04 | 1.52 | 1.98 | 1.23 | 0.18 | 0.58 | -0.35 |

Table 4: Calculated values of pressure (P) , isothermal bulk modulus ( KT ), its first pressure derivative ( ), Barton-Stacey Grüneisen parameter (γba-s) and different compressions (V/V0) for Potassium using (a) Brennan-Stacey EOS (b) Shanker EOS (c) Vinet EOS at T=T0=300K

| $V/V_0$ | P (a) | P (b) | P (c) | $K_T$ (a) | $K_T$ (b) | $K_T$ (c) | $K'_T$ (a) | $K'_T$ (b) | $K'_T$ (c) | $\gamma_{ba-s}$ (a) | $\gamma_{ba-s}$ (b) | $\gamma_{ba-s}$ (c) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.00 | 0.00 | 0.00 | 0.00 | 3.40 | 3.40 | 3.40 | 2.99 | 2.99 | 2.99 | 0.66 | 0.66 | 0.66 |
| 0.90 | 0.42 | 0.42 | 0.42 | 4.58 | 4.60 | 4.58 | 2.67 | 2.76 | 2.62 | 0.60 | 0.65 | 0.57 |
| 0.80 | 1.05 | 1.05 | 1.05 | 6.17 | 6.29 | 6.21 | 2.41 | 2.57 | 2.33 | 0.53 | 0.63 | 0.47 |
| 0.70 | 2.01 | 2.04 | 2.03 | 8.38 | 8.75 | 8.49 | 2.19 | 2.41 | 2.08 | 0.46 | 0.61 | 0.38 |
| 0.60 | 3.54 | 3.61 | 3.58 | 11.57 | 12.46 | 11.83 | 2.00 | 2.27 | 1.86 | 0.40 | 0.60 | 0.28 |
| 0.50 | 6.07 | 6.25 | 6.18 | 16.40 | 18.40 | 16.94 | 1.84 | 2.15 | 1.67 | 0.33 | 0.58 | 0.16 |
| 0.40 | 10.57 | 10.97 | 10.85 | 24.30 | 28.63 | 25.31 | 1.70 | 2.05 | 1.50 | 0.26 | 0.56 | 0.03 |
| 0.30 | 19.51 | 20.43 | 20.18 | 38.84 | 48.46 | 40.52 | 1.57 | 1.96 | 1.34 | 0.20 | 0.55 | -0.16 |
| 0.20 | 41.35 | 43.64 | 42.76 | 71.90 | 95.84 | 73.47 | 1.47 | 1.88 | 1.18 | 0.13 | 0.53 | -0.51 |

Table 5: Calculated values of pressure (P) , isothermal bulk modulus ( KT ), its first pressure derivative ( ), and Barton-Stacey Grüneisen parameter (γba-s) at different compressions (V/V0) for Rubidium using (a) Brennan-Stacey EOS (b) Shanker EOS (c) Vinet EOS at T=T0=300K

| | P | P | P | $K_T$ | $K_T$ | $K_T$ | $K'_T$ | $K'_T$ | $K'_T$ | $\gamma_{ba-s}$ | $\gamma_{ba-s}$ | $\gamma_{ba-s}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $V/V_0$ | (a) | (b) | (c) | (a) | (b) | (c) | (a) | (b) | (c) | (a) | (b) | (c) |
| 1.00 | 0.00 | 0.00 | 0.00 | 2.66 | 2.66 | 2.66 | 3.23 | 3.23 | 3.23 | 0.78 | 0.78 | 0.78 |
| 0.90 | 0.33 | 0.33 | 0.33 | 3.66 | 3.68 | 3.67 | 2.86 | 2.95 | 2.80 | 0.70 | 0.75 | 0.67 |
| 0.80 | 0.84 | 0.85 | 0.84 | 5.04 | 5.14 | 5.08 | 2.56 | 2.73 | 2.46 | 0.63 | 0.73 | 0.56 |
| 0.70 | 1.64 | 1.66 | 1.65 | 6.97 | 7.28 | 7.09 | 2.31 | 2.54 | 2.18 | 0.55 | 0.70 | 0.45 |
| 0.60 | 2.92 | 2.98 | 2.97 | 9.79 | 10.56 | 10.09 | 2.10 | 2.38 | 1.94 | 0.47 | 0.67 | 0.33 |
| 0.50 | 5.08 | 5.23 | 5.21 | 14.10 | 15.86 | 14.77 | 1.91 | 2.24 | 1.73 | 0.39 | 0.64 | 0.21 |
| 0.40 | 8.98 | 9.32 | 9.33 | 21.19 | 25.09 | 22.59 | 1.75 | 2.12 | 1.55 | 0.31 | 0.61 | 0.07 |
| 0.30 | 16.84 | 17.65 | 17.79 | 34.32 | 43.18 | 37.14 | 1.61 | 2.02 | 1.37 | 0.23 | 0.58 | -0.11 |
| 0.20 | 36.26 | 38.33 | 38.85 | 64.24 | 86.80 | 69.47 | 1.49 | 1.93 | 1.20 | 0.16 | 0.56 | -0.42 |

Table 6: Calculated values of pressure (P) , isothermal bulk modulus ( KT ), its first pressure derivative ( ), Barton-Stacey Grüneisen parameter (γba-s) and different compressions (V/V0) for Barium using (a) Brennan-Stacey EOS (b) Shanker EOS (c) Vinet EOS at T=T0=300K

| $V/V_0$ | P (a) | P (b) | P (c) | $K_T$ (a) | $K_T$ (b) | $K_T$ (c) | $K_T'$ (a) | $K_T'$ (b) | $K_T'$ (c) | $\gamma_{ba-s}$ (a) | $\gamma_{ba-s}$ (b) | $\gamma_{ba-s}$ (c) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.00 | 0.00 | 0.00 | 0.00 | 9.46 | 9.46 | 9.46 | 1.73 | 1.73 | 1.73 | 0.03 | 0.03 | 0.03 |
| 0.90 | 1.09 | 1.09 | 1.09 | 11.31 | 11.37 | 11.28 | 1.67 | 1.76 | 1.62 | 0.03 | 0.08 | 0.00 |
| 0.80 | 2.56 | 2.58 | 2.55 | 13.73 | 13.99 | 13.58 | 1.62 | 1.77 | 1.52 | 0.02 | 0.12 | -0.04 |
| 0.70 | 4.61 | 4.66 | 4.56 | 16.99 | 17.69 | 16.55 | 1.57 | 1.77 | 1.43 | 0.02 | 0.17 | -0.09 |
| 0.60 | 7.57 | 7.70 | 7.41 | 21.57 | 23.10 | 20.50 | 1.53 | 1.76 | 1.34 | 0.02 | 0.22 | -0.16 |
| 0.50 | 12.10 | 12.40 | 11.63 | 28.40 | 31.42 | 26.02 | 1.49 | 1.74 | 1.26 | 0.01 | 0.26 | -0.26 |
| 0.40 | 19.60 | 20.24 | 18.32 | 39.44 | 45.23 | 34.21 | 1.45 | 1.72 | 1.18 | 0.01 | 0.31 | -0.44 |
| 0.30 | 33.66 | 35.00 | 30.00 | 59.61 | 71.03 | 47.53 | 1.42 | 1.69 | 1.10 | 0.01 | 0.36 | -0.91 |
| 0.20 | 66.25 | 69.32 | 54.13 | 105.29 | 130.52 | 72.97 | 1.39 | 1.67 | 1.01 | 0.01 | 0.41 | -14.90 |

Table 7: Calculated values of pressure (P) , isothermal bulk modulus ( KT ), its first pressure derivative ( ), Barton-Stacey Grüneisen parameter (γba-s) and different compressions (V/V0) for Iron using (a) Brennan-Stacey EOS (b) Shanker EOS (c) Vinet EOS at T=T0=300K

| V/V0 | P (a) | P (b) | P (c) | $K_T$ (a) | $K_T$ (b) | $K_T$ (c) | $K_T'$ (a) | $K_T'$ (b) | $K_T'$ (c) | $\gamma_{ba-s}$ (a) | $\gamma_{ba-s}$ (b) | $\gamma_{ba-s}$ (c) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.00 | 0.00 | 0.00 | 0.00 | 171.11 | 171.11 | 171.11 | 7.79 | 7.79 | 7.79 | 3.06 | 3.06 | 3.06 |
| 0.90 | 27.16 | 27.21 | 27.01 | 363.12 | 364.94 | 358.38 | 6.59 | 6.69 | 5.59 | 2.76 | 2.81 | 2.20 |
| 0.80 | 90.41 | 91.05 | 88.60 | 747.67 | 763.21 | 720.74 | 5.72 | 5.90 | 4.32 | 2.45 | 2.55 | 1.62 |
| 0.70 | 237.24 | 240.97 | 228.57 | 1525.74 | 1601.24 | 1444.77 | 4.99 | 5.27 | 3.48 | 2.14 | 2.29 | 1.19 |
| 0.60 | 584.09 | 599.94 | 556.46 | 3127.24 | 3423.62 | 2963.38 | 4.34 | 4.71 | 2.88 | 1.84 | 2.04 | 0.86 |
| 0.50 | 1433.34 | 1491.04 | 1373.94 | 6514.39 | 7572.10 | 6379.67 | 3.73 | 4.21 | 2.42 | 1.53 | 1.78 | 0.60 |
| 0.40 | 3640.10 | 3836.54 | 3630.58 | 14000.06 | 17664.78 | 14888.70 | 3.15 | 3.74 | 2.05 | 1.22 | 1.52 | 0.36 |
| 0.30 | 9970.97 | 10640.80 | 10970.35 | 31863.91 | 44925.18 | 39647.84 | 2.60 | 3.30 | 1.74 | 0.92 | 1.27 | 0.15 |
| 0.20 | 31782.04 | 34290.68 | 42745.84 | 81584.71 | 133808.81 | 133421.80 | 2.08 | 2.89 | 1.46 | 0.61 | 1.01 | -0.06 |

Table 8: Calculated values of pressure (P) , isothermal bulk modulus ( KT ), its first pressure derivative ( ), Barton-Stacey Grüneisen parameter (γba-s) and different compressions (V/V0) for Molubdenum using (a) Brennan- Stacey EOS (b) Shanker EOS (c) Vinet EOS at T=T0=300K

| $V/V_0$ | P (a) | P (b) | P (c) | $K_T$ (a) | $K_T$ (b) | $K_T$ (c) | $K'_T$ (a) | $K'_T$ (b) | $K'_T$ (c) | $\gamma_{ba\text{-}s}$ (a) | $\gamma_{ba\text{-}s}$ (b) | $\gamma_{ba\text{-}s}$ (c) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.00 | 0.00 | 0.00 | 0.00 | 253.10 | 253.10 | 253.10 | 13.29 | 13.29 | 7.94 | 5.81 | 5.81 | 5.81 |
| 0.90 | 55.06 | 55.17 | 53.10 | 911.43 | 916.08 | 845.63 | 11.26 | 11.35 | 5.58 | 5.23 | 5.28 | 3.44 |
| 0.80 | 270.36 | 272.63 | 236.72 | 3146.68 | 3214.94 | 2529.88 | 9.86 | 10.05 | 4.25 | 4.65 | 4.75 | 2.26 |
| 0.70 | 1109.67 | 1131.00 | 852.30 | 10791.72 | 11363.17 | 7468.04 | 8.64 | 8.94 | 3.38 | 4.07 | 4.22 | 1.55 |
| 0.60 | 4451.31 | 4598.54 | 2994.48 | 37273.29 | 41142.44 | 22891.02 | 7.48 | 7.89 | 2.76 | 3.49 | 3.69 | 1.07 |
| 0.50 | 18266.15 | 19148 | 11143.15 | 130812 | 154670 | 76058.75 | 6.33 | 6.88 | 2.29 | 2.91 | 3.16 | 0.72 |
| 0.40 | 78788.76 | 83773 | 47078.83 | 471647 | 614677 | 288440.96 | 5.21 | 5.90 | 1.91 | 2.32 | 2.62 | 0.45 |
| 0.30 | 369859 | 398261 | 247982.04 | 1783003 | 2666097 | 1352667.04 | 4.10 | 4.95 | 1.58 | 1.74 | 2.09 | 0.21 |
| 0.20 | 2030584 | 2209197 | 1942046.91 | 7427499 | 13549880 | 9184326.57 | 3.02 | 4.04 | 13.29 | 1.16 | 1.56 | 0.00 |

Table 9: Calculated values of pressure (P) , isothermal bulk modulus ( KT ), its first pressure derivative ( ), Barton-Stacey Grüneisen parameter (γba-s) and different compressions (V/V0) for Erbium using (a) Brennan-Stacey EOS (b) Shanker EOS (c) Vinet EOS at T=T0=300K

| $V/V_0$ | P (a) | P (b) | P (c) | $K_T$ (a) | $K_T$ (b) | $K_T$ (c) | $K'_T$ (a) | $K'_T$ (b) | $K'_T$ (c) | $\gamma_{ba-s}$ (a) | $\gamma_{ba-s}$ (b) | $\gamma_{ba-s}$ (c) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.00 | 0.00 | 0.00 | 0.00 | 44.91 | 44.91 | 44.91 | 3.54 | 3.54 | 3.54 | 0.94 | 0.94 | 0.94 |
| 0.90 | 5.68 | 5.69 | 5.69 | 63.66 | 63.98 | 63.81 | 3.11 | 3.20 | 3.02 | 0.84 | 0.89 | 0.79 |
| 0.80 | 14.67 | 14.76 | 14.72 | 89.89 | 91.65 | 90.71 | 2.76 | 2.93 | 2.63 | 0.75 | 0.85 | 0.66 |
| 0.70 | 29.08 | 29.44 | 29.35 | 127.42 | 133.08 | 130.12 | 2.48 | 2.70 | 2.30 | 0.65 | 0.80 | 0.53 |
| 0.60 | 52.82 | 53.91 | 53.81 | 182.94 | 197.59 | 190.07 | 2.23 | 2.51 | 2.04 | 0.56 | 0.76 | 0.40 |
| 0.50 | 93.65 | 96.46 | 96.75 | 269.03 | 303.49 | 285.97 | 2.01 | 2.35 | 1.80 | 0.47 | 0.72 | 0.26 |
| 0.40 | 168.79 | 175.52 | 177.85 | 412.29 | 490.92 | 450.75 | 1.82 | 2.21 | 1.60 | 0.37 | 0.67 | 0.12 |
| 0.30 | 323.24 | 339.31 | 349.68 | 679.45 | 863.69 | 766.10 | 1.66 | 2.09 | 1.41 | 0.28 | 0.63 | -0.06 |
| 0.20 | 711.40 | 753.44 | 794.19 | 1291.45 | 1774.99 | 1491.48 | 1.52 | 1.99 | 1.23 | 0.19 | 0.59 | -0.34 |

The graphs plotted between Grüneisen parameter (γ) versus $V/V_0$ which are obtained by Brennan-Stacey EOS and Shanker EOS, are straight line for most of the elements except barium but it is a curved for the values obtained by Vinet EOS. It has been noted that to a good approximation the ratio γ/Ω (where $\Omega=V/V_0$) of Grüneisen parameter to volume is constant for solids [23]. Fang and Rong [24] have calculated the melting temperature under high pressure with the assumption that γ/Ω is constant, has been frequently used in work on shock compression of metals.

**Fig. (1 - 8):** The variation of Barton-Stacey Gruneisen Parameter $\gamma_{ba\text{-}s}$ versus $V/V_0$ by using Brennan-Stacey EOS, Shanker EOS and Vinet EOS for Li (bcc), Na (bcc), Rb (bcc), K (bcc), Rb (bcc), Ba (bcc), Fe (bcc), Mo (bcc), Er (bcc),

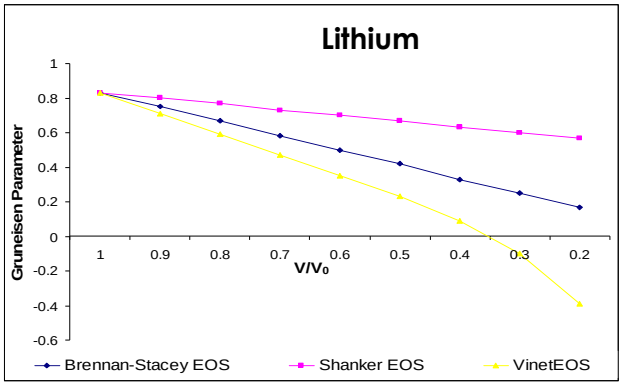


**Fig. 1**

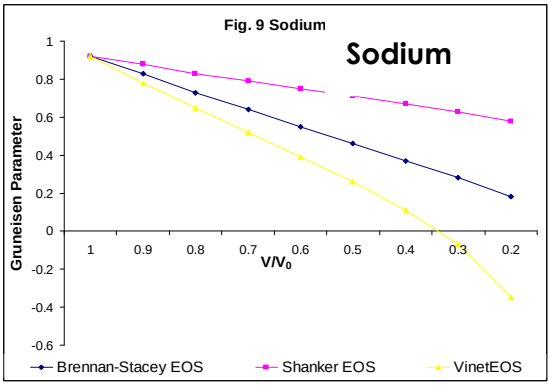


**Fig. 2**

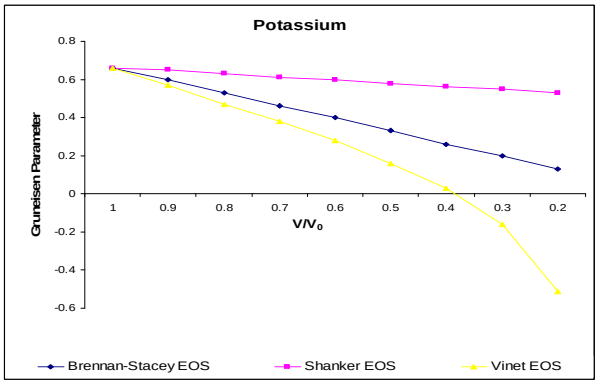


**Fig. 3**

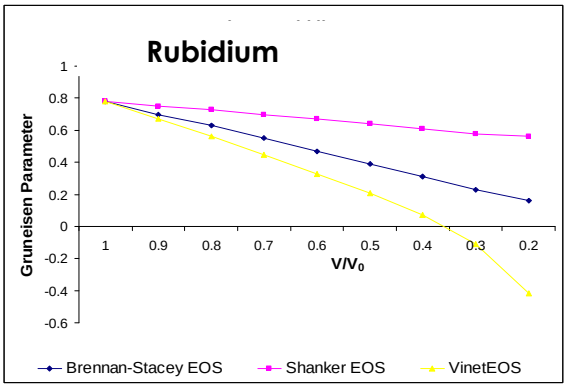


**Fig. 4**

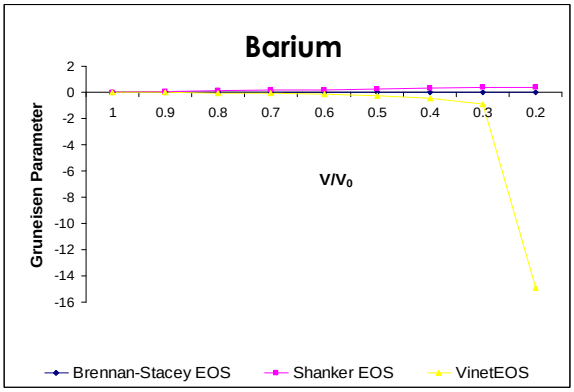


**Fig. 5**

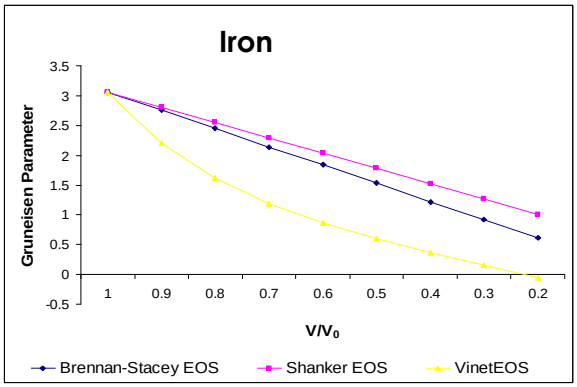


**Fig. 6**

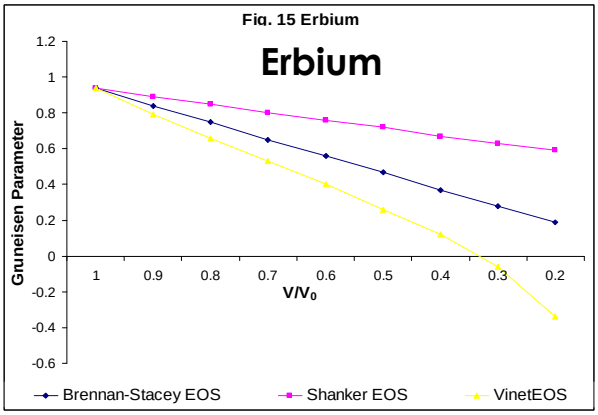


**Fig. 7**

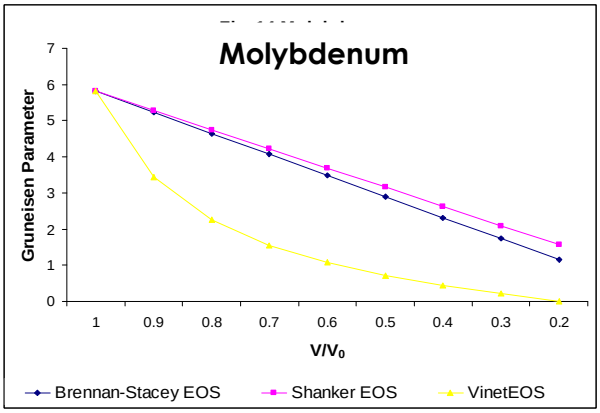


**Fig. 8**

The expression $\gamma/\Omega$ leads to equation of straight line (y=mx+c). Hence the graph between Grüneisen parameter ($\gamma$) versus $\Omega$ must be a straight line which strongly supports the Brennan-Stacey EOS and Shanker EOS both under low and high compressions where as Vinet equation is applicable only at high compression ratio. Thus, Brennan-Stacey and Shanker EOS is compatible both low and high compression ranges for calculating Grüneisen parameter whereas Vinet EOS is incompatible for calculating the Grüneisen parameter using equation (18) at low compression ranges.

In spite of this reservation on Grüneisen parameter ($\gamma$) the evidence supports the idea that the exponential variation of Grüneisen parameter ($\gamma$) with volume is much different at high pressure in comparison to low pressure. This conclusion is also supported by the work of Kopyshev [25], who investigated the behaviour of Grüneisen parameter ($\gamma$) using Fermi-Dirac theory. He found that Grüneisen parameter ($\gamma$) approached the limiting value of 1/2 at a condition of vanishing

volume. This conclusion also agrees with the results of Rice [26], by assuming that both the adiabatic bulk modulus and Grüneisen parameter (γ) are independent of temperature. He found that

$$\frac{\gamma}{V} = \frac{\gamma_0}{V_0}\left[1+\gamma_0\left(1-\frac{V}{V_0}\right)\right]^{-2}$$

Using a harmonic theory, Pastine [27] computed the curve for Grüneisen parameter (γ) versus V, which shows smaller exponent at higher pressure.

It is not always necessary to make a prior assumption of the volume dependence of Grüneisen parameter (γ) in order to compute temperature effect in shock waves. Another way tried by Takeuchi and Kanamori [28] makes an assumption about thermal equation of state, and the empirical relationship γ vs $V/V_0$ For example, Takeuchi and Kanamori [28] assumed that the γ vs $V/V_0$ curve is linear and that the pressure-energy relationship is given by one of the Mie-Grüneisen equation. It is interesting to note that the values of Grüneisen parameter (γ) computed by their method indicates that the exponential power of V for Grüneisen parameter (γ) is higher at low pressure than at high pressure. Such evidences strongly support that Grüneisen parameter calculated by using Shanker EOS is the best EOS for calculating Grüneisen parameter both at high and low compression ranges for elements.

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