Crimson Publishers
Wings to the Research

Mini Review

Analysis of the Density Dependence of the Grüneisen Parameter for Materials at High Pressures

Dwivedi A*

Department of Physics, Institute of Basic Sciences, Khandari Campus, India

ISSN: 2576-8840

Abstract

Ab initio calculations based on the density functional theory have been used to demonstrate that the Debye frequency is a linear function of density to a high accuracy for several solids under high pressures (U.C. Roy, S.K. Sarkar, Computational Condensed Matter 27 (2021) e 00552). This result has been used in the present study to demonstrate further that the Grüneisen parameter and its high order density derivatives satisfy the thermodynamic constraints for solids at high pressures in the limit of extreme compression.

Keywords: Debye frequency; Grüneisen parameter; Density; Derivatives of gamma; Infinite pressure behaviour

***Corresponding author:** Dwivedi A, Department of Physics, Institute of Basic Sciences, Khandari Campus, Agra - 282 002, India

Submission: August 13, 2022

Published: September 06, 2022

Volume 17 - Issue 5

How to cite this article: Dwivedi A. Analysis of the Density Dependence of the Grüneisen Parameter for Materials at High Pressures. Res Dev Material Sci. 17(5). RDMS. 000921. 2022.
DOI: 10.31031/RDMS.2022.17.000921

Mini Review

The Grüneisen parameter γ is of central importance for investing the thermal and elastic properties of materials [1,2]. The Grüneisen parameter is a measure of anharmonicity in the vibrational properties of a crystal. There are two versions of γ, the vibrational Grüneisen parameter γ vibrational and γ thermal [3,4]. The vibrational Grüneisen parameter $(\gamma_{vib,j})$ for a particular mode labelled by j is defined as follows [5].

$$\gamma_{vib,j} = \frac{d\ln\omega_j}{d\ln_\rho} \quad (1)$$

where ω_j is the vibrational frequency of the jth mode and ρ represents density. In the Debye model, the Debye frequency ωD is used in place of ωj, and we have the following relationship from Eq. (1)

$$\gamma_{vib} = \frac{d\ln\omega_D}{d\ln_\rho} \quad (2)$$

where γ_{vib} can now be written as γ_D.

The thermal or thermodynamic Grüneisen parameter γ_{th} is defined as follows [4]

$$\gamma_{th} = \frac{1}{C_v}\left(\frac{dP}{dT}\right)_v \quad (3)$$

where P and T denote the pressure and temperature, respectively. Cv is the ratio of the constant-volume specific heat to the volume of the material. Roy [6] have performed the vibrational spectrum first-principles electronic structure-based calculations using the Density Functional Theory (DFT) [7] as implemented in the Quantum Expresso package. These ab initio calculations reveal that the Debye frequency has a linear dependence on density to a high level of accuracy. We can write

$$\omega_D = a + b\rho \quad (4)$$

where a and b are material - dependent constants. Using Eqs. (2) and (4) we get

$$\gamma = \frac{b\rho}{a+b\rho} \quad (5)$$

Equation (5) can be rewritten as follows

$$\frac{\rho}{\gamma} = \frac{a}{b} + \rho \quad (6)$$

According to Eq. (6), the ratio of density and gamma depends linearly on density. The second order Grüneisen parameter q is defined as [1,2]

$$q = -\frac{d\ln\gamma}{d\ln\rho} \quad (7)$$

Then, Eqs. (5) and (7) yield

$$q = -\frac{a}{a+b\rho} = \gamma - 1 \quad (8)$$

It should be emphasized that at extreme compression, ρ tends to infinity, and therefore, q_∞ tends to zero, and γ_∞ tends to one.

The third order Grüneisen parameter is defined as [2]

$$\lambda = -\frac{d\ln q}{d\ln\rho} \quad (9)$$

such that

$$\frac{d\ln q}{d\ln\rho} = \frac{\rho}{q}\frac{dq}{d\rho} \quad (10)$$

Eq. (8) gives

$$\frac{q}{\rho} = -\frac{a}{\rho(a+b\rho)} \quad (11)$$

and

$$\frac{dq}{d\rho} = \frac{ab}{(a+b\rho)^2} \quad (12)$$

Then we get

$$\lambda = \frac{b\rho}{a+b\rho} \quad (13)$$

Then Eqs. (5) and (13) prove that

$$\lambda = \gamma \quad (14)$$

This is an important result according to which the third order Grüneisen parameter is equal to the first order Grüneisen parameter. Thus $\lambda_0=\gamma_0$ and $\lambda_\infty=\gamma_\infty$. Eq. (6) at initial or reference values of pressure and temperature gives

$$\frac{\rho_0}{\gamma_0} = \frac{a}{b} + \rho_0 \quad (15)$$

Eqs. (6) and (15) yield

$$\left(\frac{\rho}{\gamma} - \rho\right) = \left(\frac{\rho_0}{\gamma_0} - \rho_0\right) \quad (16)$$

Which can also be written as follows

$$\gamma = \frac{\rho\gamma_0}{\rho\gamma_0 - \rho_0(\gamma_0 - 1)} \quad (17)$$

so that

$$\gamma = 1 + \frac{\rho_0(\gamma - 1)}{\rho\left[\gamma_0 - \frac{\rho_0}{\rho}(\gamma_0 - 1)\right]} \quad (18)$$

The density ρ tends to infinity in the limit of extreme compression, Eq. (18) gives $\gamma_\infty = 1$.

Eq. (18) is useful for determining an analytical formula using the Lindemann law [8,9]

$$\frac{d\ln T_m}{d\ln\rho} = 2\left(\gamma - \frac{1}{3}\right) \quad (19)$$

Using Eq. (18) in Eq. (19), and then with respect to density, we obtain

$$\frac{T_m}{T_{m,0}} = \left(\frac{\rho}{\rho_0}\right)^{4/3}\left[\gamma_0 - \frac{\rho_0}{\rho}(\gamma_0 - 1)\right]^2 \quad (20)$$

Values of melting temperature at high pressure can be calculated with the help of Eq. (20) provided pressures corresponding to densities are known using an accurate equation of state such as the Stacey reciprocal K-primed equation [10].

The results for γ_∞, q_∞ and λ_∞ obtained in the present study are consistent with the thermodynamic constraints for solids in the limit of infinite pressure reported by Stacey [2]. According to Stacey we have $\gamma_\infty > 2/3$, $q_\infty \rightarrow 0$, and λ_∞ remains positive and finite. It has been found by Shanker et al. [11] that λ_∞ must be less than K'_∞, the pressure derivative of bulk modulus in the limit of infinite pressure. The result $\lambda_\infty = 1$ obtained in the present study is consistent with the constraint $\lambda_\infty < K'_\infty$ because K'_∞ is greater than 5/3 as derived by Stacey [2] on the basis of fundamental thermodynamics of solids.

References

1. Anderson OL (1995) Equation of state of solids for geophysics and ceramic science. Oxford University Press, New York, USA.
2. Stacey FD, Davis PM (2004) High pressure equations of state with applications to the lower mantle and core. Phys Earth Planet Inter 142(3-4): 137-184.
3. Vocadlo L, Poirer JP, Price GD (2000) Grüneisen parameters and isothermal equations of state. Am Mineral 85(2): 390-395.
4. Anderson OL (2000) The Grüneisen ratio for the last 30 years. Geophys J Int 143(2): 279-294.
5. Ashcroft N, Mermin N (1976) Solid State Physics, HRW International Editions, Holt, Rinchart and Winston.
6. Roy UC, Sarkar SK (2021) Ab initio study of the density dependence of the Grüneisen parameter at pressures up to 360 GPa. Comput Condens Matter 27: e00552.
7. Martin RM (2004) Electronic structure, basic theory and practical methods. Cambridge University Press, Cambridge, UK.
8. Lindemann FA (1910) Phys Z 11: 609.
9. Gilvarry JJ (1956) The Lindemann and Grüneisen Laws. Phys Rev 102: 308.
10. Stacey FD (2000) The K-primed approach to high-pressure equations of state. Geophysics J Int 143(3): 621-628.
11. Shanker J, Sunil K, Sharma BS (2017) The Grüneisen parameter and its higher order derivatives for the Earth lower mantle and core. Physics of the Earth and Planetary Interiors 262: 41-47.