Collective effect of size and pressure on Grüneisen parameter and Debye temperature

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Abstract

A theoretical study has been carried out on the size and pressure dependence of Debye temperature on the basis of size dependent Grüneisen parameter. The Grüneisen parameter is a dimensionless and important quantity to describe the thermodynamic and thermoelastic behaviour of solids and information about lattice anharmonicity. Debye temperature is the temperature where collective vibrations shifts to an independent thermal vibration. There exist a lot of theoretical and experimental studies on pressure dependence of Debye temperature for the bulk materials but at nano level it is very difficult to measure it. Although in recent years, many investigations have carried out on size dependent study of the Debye temperature and a decrement was observed in it with size. But pressure study of size dependent Debye temperature is still lacking. In the present work, the relation proposed by Kumari and Dass is modified for nanoparticles to study the collective effect of size and pressure on Debye temperature. The study reveals that Grüneisen parameter reduces under pressure on moving towards the nano level. Debye temperature shows enhancement for an individual particle size due to variation in unit cell parameter under pressure (up to 1 GPa). The observed results show consistency with the extracted data from experimental

studies of size and pressure dependent melting temperature. The pressure dependence of Debye temperature is vital to investigate the recoilless fraction of γ-ray emission or absorption in the Mössbauer effect.

Keywords: Grüneisen parameter, Debye temperature, Anharmonicity, Melting temperature

1. Introduction:

In today's era, the researchers have taken a lot of interest in nanocrystalline materials due to their unique properties and applications in different areas such as physics, chemistry, and materials engineering as well as in biomedical engineering. In addition to the large surface-to-volume ratios, the surface, interface, and quantum effects play a significant role which is normally inconsequent for bulk materials. Many researchers have studied theoretically and experimentally the size dependence of thermodynamic and thermoelastic properties such as melting temperature [1-4], bulk modulus [5-6], specific heat [7-8], melting entropy and enthalpy [9-10], Debye temperature [11-12] and Grüneisen parameter [13] of nanomaterials.

Grüneisen parameter (γ) belongs to the most important characteristics of crystal lattice dynamics [14]. It enters into the equation of state to represent the measurement of the anharmonicity of the forces acting in a crystal and reflects the features and characteristics of the distribution of the frequencies of the phonon spectrum and their variations under pressure [15]. Debye temperature is the temperature of a crystal's highest normal mode of vibration, i.e., the highest temperature that can be achieved due to a single normal vibration which is closely connected with properties like specific heat,

thermal expansion, and vibrational entropy. Generally, the thermodynamic properties under pressure are very important. Significant numbers of studies have been done on the pressure dependence of Debye temperature and Grüneisen parameter for bulk materials [16-21]. However, to the best of our knowledge, the combined study of size and pressure on Debye temperature and Grüneisen parameter have not been done yet. In the present work, the effort is taken to study the collective effect of size and pressure on the Grüneisen parameter and Debye temperature. Initially the size dependency of Grüneisen parameter is checked by modifying the bulk definition for nanoparticles and then for size and pressure dependency is observed for Grüneisen parameter and Debye temperature by modifying the relations given by Kumar and Dass for nanoparticles.

2. Methods:

2.1 Size and pressure dependent Grüneisen parameter:

Grüneisen parameter can be defined macroscopically in terms of thermodynamic properties such as heat capacity, thermal expansion, and isothermal bulk modulus. Experimental determination of Grüneisen parameter is extremely difficult therefore a theoretical expression is modified for nanoparticles.

$$\gamma_n = \frac{\alpha_{0n} K_{0n} V_n}{C_n} \quad (1)$$

In the present study, the product of volume thermal expansion coefficient (α_{0b}) and isothermal bulk modulus (K_{0b}) is considered to be constant for nano and their bulk counterpart respectively ($\alpha_{0b}K_{0b} = \alpha_{0n}K_{0n}$) [14] and γ_n, V_n, and C_n represent the Grüneisen parameter, molar volume and molar specific heat capacity for nanomaterials respectively.

In the present work, the unit cell structure is assumed cubic for nanoparticles. With the help of the expression given by Qi and Wang (2003) [22] for the variation of lattice parameter of an ideal crystal with size the molar volume for nanoparticles can be defined as;

$$V_n = \left(\frac{GD}{E_S + GD}\right)^3 V \tag{2}$$

Where, G, V and E_S denote the shear modulus, molar volume and surface energy of bulk material respectively. D denotes the diameter of nanoparticles.

The expression for the specific heat of nanomaterials is developed by combining the Qi's model of melting [23] with the expression of specific heat given by Bhatt *et al*. [24] as;

$$\frac{C_n}{C_b} = \left(1 - \frac{T_0}{T_{mb}}\right)\left[1 - \frac{T_0/T_{mb}}{\left(1 - \frac{2d}{D}\right)}\right]^{-1} \tag{3}$$

Where, C_b and T_{mb} denote the molar specific heat capacity and melting temperature of the bulk material respectively. d and T_0 represent the atomic diameter of nanoparticles and reference temperature respectively.

Putting eq. (2) and (3) in eq. (1), the expression for size dependent Grüneisen parameter can be given as;

$$\gamma_n = \frac{\alpha_{0n} K_{0n} \left(\frac{GD}{E_S + GD}\right)^3 V}{C_b\left(1 - \frac{T_0}{T_{mb}}\right)\left[1 - \frac{T_0/T_{mb}}{\left(1 - \frac{2d}{D}\right)}\right]^{-1}} \tag{4}$$

For the pressure dependence of Grüneisen parameter, the relation derived by Kumari and Dass [17] for bulk materials is modified for nanoparticles as;

$$\gamma_n(P) = \gamma_n - \eta P \tag{5}$$

$\gamma_n(P)$ represents the size and pressure dependent Grüneisen parameter. P denotes the applied pressure. η is pressure independent parameter and is defined as [25];

$$\eta = \frac{\beta_T - \beta_S}{T_0 \alpha_{0b} K_{0b}} \quad (6)$$

β_T and β_S are first-order derivatives of isothermal and adiabatic bulk moduli at constant pressure respectively and their difference is approximately equal to 0.1 [14].

Finally putting the value of size dependent Grüneisen parameter and η for nanoparticles given by eq. (4) and eq. (6) in eq. (5), the size and pressure dependent equation for Grüneisen parameter can be expressed as;

$$\gamma_n(P) = \frac{\alpha_{0n} K_{0n} \left(\frac{GD}{E_S + GD}\right)^3 V}{C_b \left(1 - \frac{T_0}{T_{mb}}\right) \left[1 - \frac{T_0 / T_{mb}}{\left(1 - \frac{2d}{D}\right)}\right]^{-1}} - \eta P \quad (7)$$

2.2 Size and pressure dependent Debye temperature:

On the basis of Grüneisen parameter, Kumari and Dass (1986) [17] derived the relation for the pressure dependence of Debye temperature for bulk materials. For nanoparticles the expression is modified as;

$$\frac{\theta_{Dn}(P)}{\theta_{Dn}(0)} = \left(1 + \frac{\gamma_n P}{K_{0n}}\right) \quad (8)$$

Where $\theta_{Dn}(P)$ denotes pressure and size-dependent Debye temperature, and $\theta_{Dn}(0)$ represents the size-dependent Debye temperature at zero pressure. Size dependent bulk modulus has been given by Kumar and Kumar (2010) [26] as; $K_{0n} = K_{0b}\left(1 - \frac{2d}{D}\right)$. After incorporating the values of size dependent Grüneisen parameter (γ_n) (using equation 4) and bulk modulus (K_{0n}) we get the final expression for collective effect of size and pressure on Debye temperature as equation (9).

$$\frac{\theta_{Dn}(P)}{\theta_{Dn}(0)} = \left(1 + \frac{\left(\frac{\alpha_{0n} K_{0n} \left(\frac{GD}{E_S + GD} \right)^3 V}{C_b \left(1 - \frac{T_0}{T_{mb}} \right) \left[1 - \frac{T_0 / T_{mb}}{\left(1 - \frac{2d}{D} \right)} \right]^{-1}} \right) P}{K_{0b} \left(1 - \frac{2d}{D} \right)} \right) \quad (9)$$

As the experimental studies for the pressure effect on Debye temperature for nanoparticles are lacking, therefore size and pressure dependent Debye temperature are extracted from the pressure dependent experimental studies of melting temperature for nanomaterials to show the consistency of the proposed equation. For this, the Lindemann's theory of melting for bulk materials [27] is used and modified.

At zero pressure: $T_{mn}(0) \propto V_{0n}^{\frac{2}{3}} \{\theta_{Dn}(0)\}^2$ (10)

At pressure P: $T_{mn}(P) \propto V_n^{\frac{2}{3}} \{\theta_{Dn}(P)\}^2$ (11)

Combining equations (10) and (11) we get the size and pressure dependent Debye temperature as;

$$\frac{\theta_{Dn}(P)}{\theta_{Dn}(0)} = \sqrt{\frac{T_{mn}(P)}{T_{mn}(0)} \left(\frac{V_0}{V} \right)_n^{2/3}} \quad (12)$$

Where $T_{mn}(P)$ represents the size and pressure dependent melting temperature and $T_{mn}(0)$ represents the size dependent melting temperature at zero pressure. $(V/V_0)_n$ is volume compression for nanomaterials, calculated with the help of Birch-Murnaghan EOS [28] which is modified for nanomaterials by including size dependent bulk modulus and can be written as;

$$P = \frac{3}{2} K_{0b} \left(1 - \frac{2d}{D} \right) \left[\left(\frac{V_0}{V} \right)_n^{7/3} - \left(\frac{V_0}{V} \right)_n^{5/3} \right] \quad (13)$$

Here in the present study, first order pressure derivative of bulk modulus is considered to be constant ($K_0' = 4$).

3. Results and Discussion:

Under pressure, the mechanical and thermodynamic properties change so high pressure study is essential to understand the applications of materials. Pressure influenced properties of the materials are of great importance in many applications [29-30] like pressure dependent Debye temperature is very important to study the recoilless fraction in Mössbauer experiment [17]. Therefore, in the present work, size dependent Debye temperature as a function of pressure has been studied for two nanometals Al and Pb, with the help of size dependence of Grüneisen parameter and bulk modulus. In the quasi-harmonic Debye model, the Grüneisen parameter is of great significance. It describes the anharmonic effect of the crystal lattice thermal vibration and has been widely used to characterize the thermodynamic behaviour of a material under pressure. In the present study the size dependence of Grüneisen parameter is understood with the help of the equation (4). Figure 1 [(a) and (b)] represent the variation of Grüneisen parameter with size for Al and Pb nanoparticles respectively. Grüneisen parameter shows decrement with the decrease in size of the nanoparticle. On moving towards the nano level, the reduction in lattice parameter [22] and enhancement in specific heat [24] result in the decrement in Grüneisen parameter. The same decreasing behaviour is also noticed in the previous theoretical study [13]. The collective effect of size and pressure on Grüneisen parameter is also studied with the help of equation (7). Figure 2[(a)

and (b)] show the variation of Grüneisen parameter with pressure (up to 1 GPa) for Al (37 nm) and Pb (6.7 nm) respectively. It reveals that the Grüneisen parameter decreases with pressure for a particular size of nanoparticles. Anharmonic effects are expected to strongly decrease when pressure increases. This is due to an extension of the temperature domain where zero-point vibrations are larger than thermal vibrations. The pressure variation of size dependent Debye temperature for Al (37 nm) and Pb (6.7 nm) is calculated with the help of equation (9) and the obtained results are demonstrated in Figure 3[(a) and (b)] respectively. The results are in close agreement with the available experimental data extracted from the size and pressure dependent melting temperature [31, 32] by modifying Lindemann's theory of melting for size and pressure dependent melting temperature given as eq. (12). It is found that the Debye temperature increases with increasing pressure linearly as also observed in the bulk materials at a given temperature [17-18]. The most predominant effect caused by applied external pressure is the stiffening of the lattice [33]. A change in crystal volume would naturally affect the frequencies of the normal modes of vibrations. At Debye temperature the wavelength of the phonon vibrations is comparable to the lattice parameter [34]. Under the effect of pressure, the frequency of vibrations increases results in enhancement of Debye temperature.

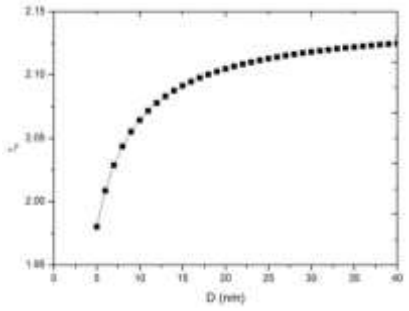
4. Conclusion:

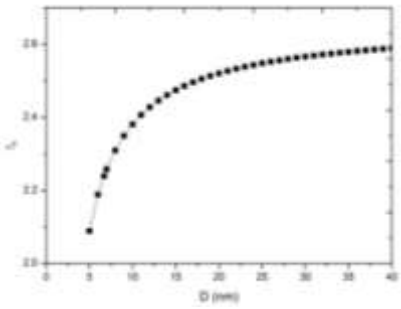
A collective study of size and pressure on Grüneisen parameter and Debye temperature is done on the basis of the quasi-harmonic Debye model. Results show that Grüneisen parameter decreases with decreasing size due to

decrement in lattice constant and increment in specific heat. Pressure dependent Grüneisen parameter decreases linearly with pressure for a particular size. Size-dependent Debye temperature increases due to increment in the frequency of lattice vibrations when external pressure is applied. Pressure-dependent Debye temperature is used to calculate the recoil-free fraction in Mössbauer effect which is useful to probe the tiny changes in the energy levels of an atomic nucleus.

Table 1: Input parameters used for the present study

Input Parameters	**Al**	**Pb**
Atomic diameter (d)	0.246 nm [38]	0.35 nm [36]
Specific heat (C_b)	24.3 J/mol/K [39]	26.9 J/mol/K [39]
Surface energy (E_s)	1.16 J/m^2 [37]	0.593 J/m^2 [37]
Coefficient of thermal expansion (α)	23.1*10^{-6} K^{-1} [35]	28.9*10^{-6} K^{-1} [35]
Bulk modulus (K_{0b})	75.2 GPa [35]	45.8 GPa [35]
Molar volume (V)	10 cm^3/mol [35]	18 cm^3/mol [35]
Shear modulus (G)	26 GPa [35]	5.59 GPa [35]
Bulk Melting temperature (T_{mb})	933.47 K [36]	600.61 K [36]

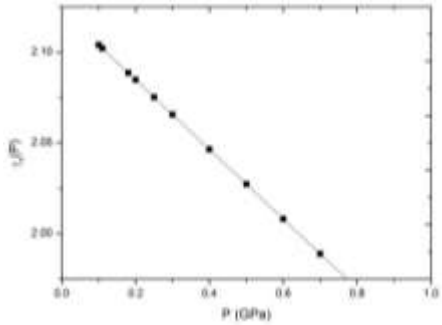


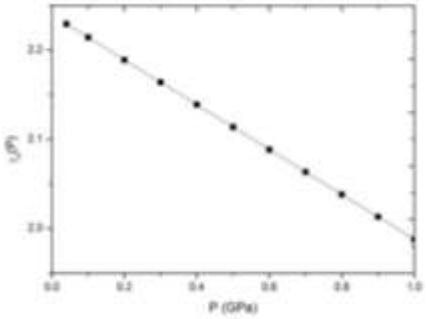


1(a) 1(b)

Fig. 1: Variation of Grüneisen parameter with size for (a) Al and (b) Pb

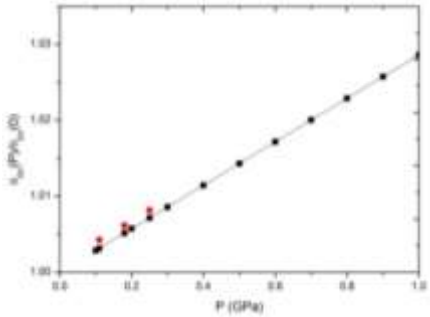
nanoparticles respectively

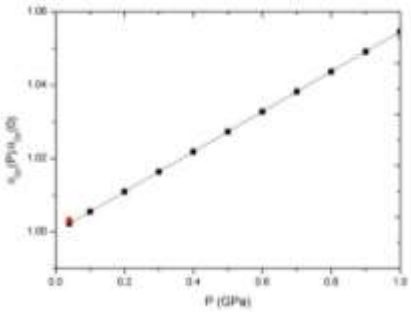




2(a) 2(b)

Fig. 2: Variation of Grüneisen parameter with pressure for (a) Al (37 nm) and (b) Pb (6.7 nm) nanoparticles respectively





3(a) 3(b)

Fig. 3: Variation of Debye temperature ratio with pressure for (a) Al (37 nm) and (b) Pb (6.7 nm) nanoparticles respectively

*In the above figures black symbols denote the calculated values of Debye temperature ratio by eq. () while the red symbols represent the calculated values by eq. (12) in which size and pressure dependent melting temperature is extracted from the available experimental data [31-32].

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