Grüneisen parameter and Debye temperature under the combined influence of size and pressure

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Abstract

A theoretical investigation has been conducted to examine the impact of size and pressure on the Debye temperature, utilizing a size-dependent Grüneisen parameter. The Grüneisen parameter, a dimensionless and crucial parameter, serves as a representation of the thermodynamic and thermoelastic characteristics of solids, offering insights into lattice anharmonicity. The Debye temperature signifies the point at which collective vibrations transition to independent thermal vibrations. While there exists an abundance of theoretical and experimental research on the pressure dependence of Debye temperature in bulk materials, measuring it at the nanoscale presents challenges. In recent years, numerous studies have explored the size-dependent variations in the Debye temperature. However, the investigation into the combined effects of size and pressure on the Debye temperature has remained unexplored until now.

In this study, the research conducted by Kumari and Dass has been utilized to examine the combined impact of size and pressure on the Debye temperature for nanoparticles. The findings reveal a reduction in the Grüneisen parameter under pressure at the nanoscale. Furthermore, the Debye temperature exhibits enhancement for a specific particle size due to variations in the unit cell parameter under pressure, particularly up to 1 GPa. These outcomes align consistently with data extracted from experimental studies on the melting temperature, which is dependent on both

size and pressure. Understanding the pressure dependence of the Debye temperature is essential for observing the recoilless fraction of γ-ray emission or absorption in the Mössbauer effect.

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

1. Introduction:

Nanomaterials have become important in today's time due to their distinctive properties and several applications in different areas such as physics, chemistry, engineering and biomedicine etc. Along with the large surface-to-volume ratio, surface, interface, and quantum effects play a significant role which is usually 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) is one of the most important characteristics of crystal lattice dynamics [14]. It represents the measurement of the anharmonicity of the forces acting in a crystal into an equation of state and reflects the characteristics of the phonon spectrum frequency distribution and their variation with pressure [15]. Debye temperature is closely associated with the properties such as thermal expansion, specific heat and vibrational entropy and can be defined as the temperature of crystal's highest normal mode of vibration, i.e., the maximum temperature that can be attained by an individual normal vibration. Generally, the thermodynamic properties under pressure are very important. There exists a number of studies on the pressure dependent Debye temperature and Grüneisen parameter for bulk materials [16-21]. To the best of our knowledge, there has been

no comprehensive investigation into the simultaneous influence of size and pressure on the Debye temperature and Grüneisen parameter. This study seeks to bridge this gap by examining the combined impact of size and pressure on both the Grüneisen parameter and Debye temperature.

The initial step involves assessing the size-dependent behaviour of the Grüneisen parameter by adapting the conventional definition used for bulk materials to the context of nanoparticles. Subsequently, the study extends to investigate the dependencies on size and pressure for both the Grüneisen parameter and Debye temperature, employing modifications to the equations provided by Kumar and Dass specifically tailored for nanoparticles.

Methods:

2.1 Size and pressure dependent Grüneisen parameter:

The Grüneisen parameter, at the macroscopic level, is typically expressed in relation to thermodynamic characteristics like heat capacity, thermal expansion, and isothermal bulk modulus. However, experimentally measuring the Grüneisen parameter poses challenges, especially for nanoparticles. Consequently, a theoretical expression has been adapted to address this issue.

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

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 this work, the unit cell structure is assumed cubic for nanoparticles. Using 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;

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

In this context, G represents the shear modulus, V stands for the molar volume, and E_S represents the surface energy of the bulk material. D, on the other hand, signifies the diameter of nanoparticles.

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

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

Where, C_b and T_{mb} denote the molar specific heat capacity and melting temperature of the bulk material respectively. d and T_0represent the atomic diameter of nanoparticles and reference temperature respectively.

Putting eq. (2) and (3) in eq. (1), The equation describing the size-dependent Grüneisen parameter can be formulated as follows:

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

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

$$\gamma_n(P) = \gamma_n - \eta P \quad (5)$$

$\gamma_n(P)$ 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:

Based on the Grüneisen parameter, Kumari and Dass (1986) [17] established a relationship describing the pressure-dependent Debye temperature for bulk materials. For nanoparticles, this expression is adapted as follows:

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

Where $\theta_{Dn}(P)$represents 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 including the values of size dependent Grüneisen parameter (γ_n) (using equation 4) and bulk modulus (K_{0n}) we get the final expression for combined 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 $T_{mn}(P)$ indicates 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;

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

In this current investigation, we assume that the first-order pressure derivative of the bulk modulus remains constant (i.e., $K'_0 = 4$).

2. Results and Discussion:

Under pressure, the mechanical and thermodynamic properties change so high-pressure study is necessary 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]. Hence, in this research, we have examined the pressure-dependent size-specific Debye temperature for two nanoscale metals, namely aluminium (Al) and lead (Pb), utilizing the size-related variations in the Grüneisen parameter and bulk modulus. In the quasi-harmonic Debye model, the Grüneisen parameter is of great significance. It depicts the anharmonic effect of the crystal lattice thermal vibration and has been extensively used to describe 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 influence of both size and pressure on the Grüneisen parameter is also investigated using the provided 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. With increase in pressure, it is expected that anharmonic effects decrease because of an expansion of the temperature domain where zero-point vibrations are greater 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 linearly with increasing pressure 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 equivalent to the lattice parameter[34]. Under the effect of pressure, there is an increase in the frequency of vibrations which results in increase of Debye temperature.

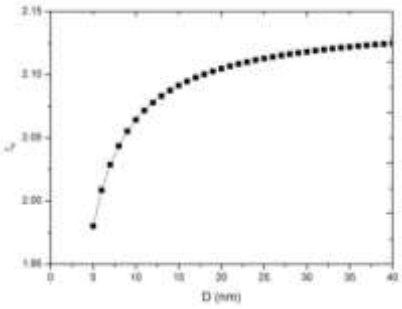
3. Conclusion:

A comprehensive investigation of the combined influence of size and pressure on the Grüneisen parameter and Debye temperature has been conducted, employing the quasi-harmonic Debye model. The results affirm that the Grüneisen parameter diminishes as size decreases, primarily owing to a reduction in the lattice constant and an increase in specific heat. Additionally, the pressure-dependent Grüneisen parameter exhibits a linear decrease with increasing pressure, maintaining a constant size. Simultaneously, the size-dependent Debye temperature experiences an enhancement due to the increased vibrational frequency of the lattice when external pressure is

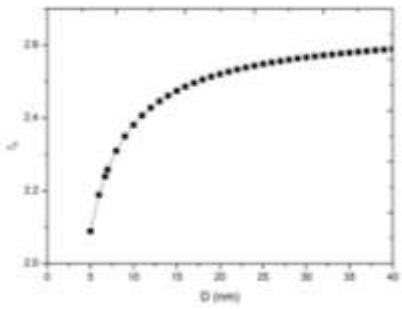
applied. This pressure-dependent Debye temperature is subsequently employed in calculating the recoil-free fraction in the Mössbauer effect, a valuable tool for investigating minuscule variations in the energy levels of atomic nuclei.

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]	26.9J/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]

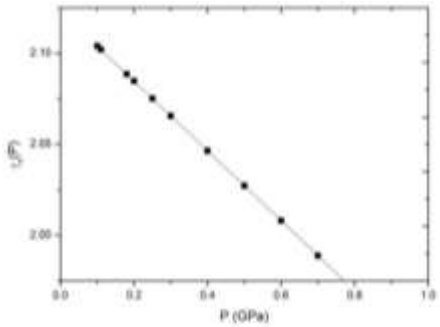


1(a)

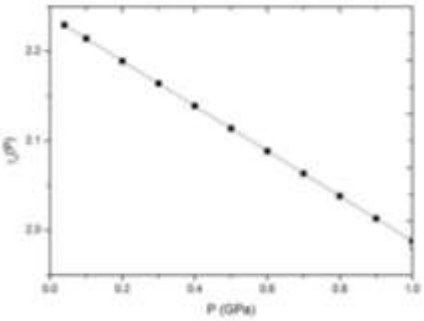


1(b)

Fig. 1: Variation in the Grüneisen parameter concerning size is presented for (a) aluminum (Al) and (b) lead (Pb) nanoparticles, respectively.

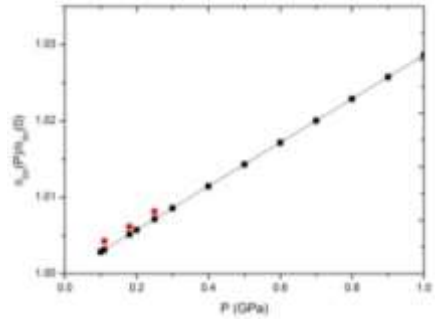


2(a)

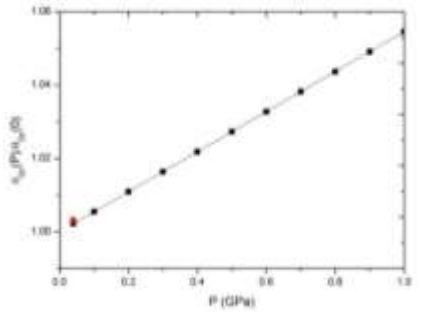


2(b)

Fig. 2: The change in the Grüneisen parameter with pressure is examined for (a) aluminum (Al) nanoparticles with a size of 37 nm and (b) lead (Pb) nanoparticles with a size of 6.7 nm, 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. (9) while the red symbols represent the calculated values by eq. (12) in whichsize and pressure dependent melting temperature is extracted from the available experimental data [31-32].

References

[1]Lai, S.L., Guo, J.Y., Petrova, V., Ramanath, G. & Allen, L.H. Size-Dependent Melting Properties of Small Tin Particles :Nanocalorimetric Measurements. *Phys. Rev. Lett.***77**(1) (1996) 99–102. DOI: 10.1103/PhysRevLett.77.99.

[2]Buffat, Ph. & Borel, J.-P. Size effect on the melting temperature of gold particles. *Phys. Rev. A***13**(6) (1976) 2285-2297. DOI: https://doi.org/10.1103/PhysRevA.13.2287.

[3]Olson, E.A., Efremov, M.Y., Zhang, M., Zhang, Z. &Allen, L.H. Size-dependent melting of Bi nanoparticles. *J. Appl. Phys.***97**(3)(2005) 034304 (1–9). DOI: https://doi.org/10.1063/1.1832741.

[4]Arora, N. & Joshi, D.P. A theoretical approach to study the melting temperature of metallic nanowires. In: AIP Conf. Proc. DAE Solid State Physics Symposium **1731** (2015) 050054(1-3). DOI:10.1063/1.4947708.

[5]Gu, Q.F., Krauss, G. & Steurer, W. Unexpected High Stiffness of Ag and Au Nanoparticles. *Phys. Rev. Lett.***045502** (2008) 1–4. DOI: https://doi.org/10.1103/PhysRevLett.100.045502.

[6]Bhatt, J.C. &Kholiya, K. Effect of size on the elastic and thermodynamic properties of nanomaterials. *I.J.P.A.P.***52**(9) (2014) 604–608.

[7]Gafner, Y.Y., Gafner, S.L., Zamulin, I.S., Redel, L.V. &Baidyshev, V.S. Analysis of the Heat Capacity of Nanoclusters of FCC Metals on the Example of Al, Ni, Cu, Pd, and Au. *Phys. Met.Metallog.***116**(6) (2015) 568-575. DOI: https://doi.org/10.1134/S0031918X15040055.

[8]Wang, L., Tan, Z., Meng, S., Liang, D. & Li, G. Enhancement of molar heat capacity of nanostructuredAl_2O_3. *J.NanoParticle Res.***3** (2001) 483–487.

[9]Fu, Q., Zhu, J., Xue, Y. & Cui, Z. Size- and shape-dependent melting enthalpy and entropy of nanoparticles. *J. Mater. Sci.***52**(4) (2016) 1911-1918. DOI: 10.1007/s10853-016-0480-9.

[10]Singh, M., Lara, S. & Tlali, S. Effects of size and shape on the specific heat, melting entropy and enthalpy of nanomaterials. *J. Taibah. Univ. Sci.* **11**(6)(2016) 922–929. DOI: https://doi.org/10.1016/j.jtusci.2016.09.011.

[11]Balerna, A. &Mobilio, S. Dynamic properties of Debye temperatures of bulk Au and Au clusters studied using extended X-ray-absorption fine-structure spectroscopy. *Phys. Rev. B***34**(4) (1986)2293-2298.

[12]Arora, N., Joshi, D.P. &Pachauri U. Size and shape dependent Debye temperature of Nanomaterials. *ScienceDirect Mater Today: Proc.***4**(9) (2017) 10450–10454. DOI: https://doi.org/10.1016/j.matpr.2017.06.398.

[13]Abdullah, B.J. & Omar, M.S. Grüneisen Parameter and Its Related Thermodynamic Parameters Dependence on Size of Si Nanoparticles. *Z.J.P.A.S.***28**(4) (2016) 126-132. DOI: https://doi.org/10.21271/ZJPAS.28.4.17.

[14]Anderson, O.L. Equations of state of solids for geophysics and ceramic science, New York, Oxford University Press (1994).

[15]Liu, Q. & Chen, L.R. Pressure dependence of the Grüneisen parameter and thermal expansion coefficients of solids. *I.J.P.A.P.***55** (2017) 368-371.

[16]Sirdeshmukh, D.B. &Subhadra, K.G. The pressure dependence of Debye temperatures of alkali halides. *Phys. Stat. sol. (b)***150**(1988) K11-K14.

[17]Kumari, M. On the Pressure Dependence of Grüneisen Parameter in solids. *Phys. Stat. sol. (b)***133**(1986) 101-110.

[18]Fang, Z.-H. On the Pressure Dependence of the Debye Temperature in Solids. *Phys. Stat. sol. (b)***222** (2000) 451-456.

[19]Barton, M.A. &Stacey, F.D. The Grüneisen parameter at high pressure: a molecular dynamical study. *Phys. Earth Planet. In.***39** (1985) 167-177.

[20]Fang, Z.-H. Pressure dependence of Grüneisen parameter in solids. *Phys. Stat. sol. (b)***197 (**1996) 39-43.

[21]Rai, H.K., Shukla, S.P., Mishra, A.K. &Pandey, A.K. Pressure dependence of Grüneisen parameter of some transition metals. *J. Chem. Pharm. Res.***2**(4) (2010) 343-356.

[22]Qi, W.H. &Wang, M.P. Size and shape dependent melting temperature of metallic nanoparticles. *Mater. Chem. Phys.***88**(2–3) (2004) 280–284. DOI: 10.1016/j.matchemphys.2004.04.026.

[23]Qi, W.H. Size effect on melting temperature of nanosolids. *Phys. B***368** (2005) 46–50. DOI: 10.1016/j.physb.2005.06.035.

[24]Bhatt, S., Kumar, R. & Kumar, M. Specific heat and thermal conductivity of nanomaterials. *Mod. Phys. Lett. B***1750011** (2017) 1–13. DOI: 10.1142/S0217984917500117.

[25]Dixit, S. & Shanker, J. On the pressure and volume dependence of the Grüneisen parameter and Debye temperature for NaCl crystals. Phys. Stat. Sol. (b) **187**(1995) 497-500.

[26]Kumar, R. & Kumar, M. Size dependence of thermoelastic properties of nanomaterials. *Int. J.Nanosci.***9**(5) (2010) 537-542. DOI: 10.1142/S0219581X10007113.

[27]Lindemann, F.A. The calculation of molecular vibrational frequencies. *Phys. Z.***11** (1910) 609-612.

[28]Birch, F. Finite Elastic Strain of Cubic Crystals. *Phys. Rev.* **71**(11)1947809-824. DOI: 10.1103/physrev.71.809.

[29]Obiekea, K., Aku, S.Y. &Yawas, D.S. Influence of pressure on the mechanical properties and grain refinement of die cast aluminum A1350 alloy. *Pelagia Research Library Adv. Appl. Sci. Res.***3**(6) (2012) 3663-3673.

[30]de Freitas, C.R.D., de Góis, M.M., Da Silva, R.B., da Costa, J.A.P. & Soares, J.M. Influence of pellet compaction pressure on the physical properties of $La_{0.7}Ba_{0.3}Mno_3$manganite. *Mater. Res.***21**(1) (2018) 1–7. DOI: https://doi.org/10.1590/1980-5373-MR-2017-0197.

[31]Mei, Q.S, Wang, S.C., Cong, H.T., et al. Pressure induced superheating of Al nanoparticles encapsulated in Al_2O_3 shells without epitaxial interface. *Acta. Mater.***53 (**2005) 1059-1066. DOI: 10.1016/j.actamat.2004.11.003.

[32]Wang, H. & Zhu, H. Melting of Pb nanocrystals embedded in Al, Si, and Cu matrices. *Nano. Res. Lett.***10** (2015) 487. DOI: 10.1186/s11671-015-1196-5.

[33]Suleiman, B.M., Gustafsson, S.E. & Lunden, A. Uniaxial Pressure Dependence of the Debye Temperature in Metals. *Int. J.Thermophysi.***18**(6) (1997) 1527-1537.

[34]Garai, J. Physics behind the Debye temperature. arXiv:physics/0703001[physics.chem-ph].

[35]Brandes, E.A. & Brook, E.B. Smithells metals reference book, butterworths, London, 7th Ed. (1983).

[36]Mirjalili, M. &Khaki, J.V. Prediction of nanoparticles size-dependent melting temperature using mean coordination number concept. *J. Phys. Chem. Sol.***69**(2008) 2116-2123. DOI: 10.1016/j.jpcs.2008.03.014.

[37]Tyson, W.R. & Miller, W.A. Surface free energies of solid metals estimation from liquid surface tension measurements. *Surf. Sci.***62 (**1977) 267-276. DOI: 10.1016/0039-6028(77)90442-3.

[38]Li, Y.J., Qi, W.H., Huang, B.Y., et al. Modeling the melting temperature of metallic nanowires. *Mod. Phys. Lett. B***24** (2010) 2345 -2356. DOI: 10.1142/S0217984910024699.

[39]Kittel, C. Introduction to Solid State Physics. 5th ed. Wiley. New York. (1976).