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Research paper

A bond energy theory to analysis the melting temperature and Debye temperature of nanoscale solids

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Abstract

Based on bond theory model and surface effects, a size dependent theory is discussed to study the melting temperature and Debye temperature of nanoscale materials. The number of atoms on the surface to the total number of atoms in nanosolid is analysed in terms of size and shape factor of nanomaterials. The variation of melting temperature and Debye temperature is reported for spherical, tetrahedral, hexahedral and octahedral shapes nanomaterials. It is found that the melting point and Debye temperature decrease as the particle size is reduced. The results studied are compared with the available experimental and simulation data. A good agreement between the present calculated results and the results reported by earlier scholars confirm the strength of the theory.

Keywords: *Bond Energy; Debye Temperature; Melting Entropy; Surface Effect; Nanomaterials*.

1. Introduction

The physical properties of nanoscale solids depend upon their size because of the maximum fraction of uncoordinated atoms on their surface. The nanomaterials differ from the corresponding bulk of the material due to their small size. The shape and size dependent thermodynamical properties like melting point, cohesive energy, Debye temperature, surface energy and specific heat have created keen interest in scientific and technological fields [1-5]. From these properties of nanosolids, the Debye temperature of the nanosolids has received the considerable notice, because it is an essential physical quantity to characterize many material properties, as the thermal vibration of atoms and phase transitions. Debye–Einstein approximation model is used to calculate nanoscale size-dependent values of Gruneisen parameters, specific heat capacity and Debye temperature for Si nanowires [6] and it is reported that the Debye temperature decreases with the decrease of the nanowires' diameter. Experimentally, it is reported that the cohesive energy of the nanosolids is fairly lower than that of corresponding bulk materials. Researchers have developed a generalized bond energy model to calculate the cohesive energy of nanoparticles by considering the different contribution of face, edge and corner atoms [7, 8]. It is shown that the cohesive energy decreases with decrease the size, whereas its bulk counterparts are constants at a given temperature. The melting points depression and enhancement have been shown to depend on size. Dimension and the surface conditions of the nanosolids and the melting of the metallic nanosolids have been explored both experimentally and theoretically. The theoretical model was first proposed in 1909, which was based on equating the Gibbs free energies of solid and liquid spherical nanosolids. In the bond energy model, atoms of the nanoparticles are classified as interior and exterior atoms. Truly, the cohesive energy of a material is the energy needed to divide the material into isolated atoms; the straight result of cohesive energy is to create a new surface. The enlarged surface energy should equal the cohesive energy of the material, which results from the surface difference between the total atoms and the materials. The cohesive energy of the nanoparticle is due to the contribution of both interior and exterior atoms. It is discussed that the interior atoms are the same as those of bulk materials, and the exterior atoms have large dangling bonds. Different models have been developed to calculate the size dependence cohesive energy such as liquid drop model, latent heat model and bond energy model [9-10].

Since the properties of solids relate to the bonding between atoms, whereas the bonding is characterized by cohesive energy. The atomic cohesive energy determines the thermodynamical properties. It has been reported that the melting temperature of In nanomaterials embedded in an Al matrix changes with decreasing particle size [11].

So far the analytical study of the literature reveals that number of experimental work has been done to calculate the melting point and Debye temperature. Although size effects on all the above physical properties have been modelled independently by a chain of related theoretical lines, consistent understanding and a systematically thermodynamical conduct considering both the size and the surface effects are highly required in order to disclose the physical nature of the nanosolids. Some efforts, based on potential approach and simulation are made by earlier workers. In the present paper, we used the bond theory model [12] and studied a very simple theory to analysis the melting temperature and Debye temperature of nanomaterials.

2. Theoretical formulation

The cohesive energy of the metallic nanoparticles is the sum of the bond energy of all the atoms. It is well known that the cohesive energy is an important factor to calculate the metallic bond, which equals to the energy that can divide the metal into isolated atoms by destroying all metallic bonds. The metallic bonds of each atoms equal to the sum of interaction energies between the atom and the other atoms. In other words, each interior atom forms bonds

with the surrounding atoms. The cohesive energy of a metallic crystal in any shape can be written as [13].

$$E_c(r) = \frac{1}{2} E_{bond} \left[\frac{1}{4} \beta 4\gamma \frac{R^2}{r^2} + \beta \left(\frac{R^3}{r^3} - 4\gamma \frac{R^2}{r^2} \right) \right] \quad (1)$$

where, E_{bond} is the bond energy and β is the number of bonds as every interior atom creates bonds with the surrounding atoms. Here, the factor ½ is due to that each bond belongs to two atoms. On simplification, relationship (1) may be written as

$$E_c(r) = \frac{1}{2} n \beta E_{bond} \left[1 - 6\gamma \frac{r}{2R} \right] \quad (2)$$

where, $n = R^3 / r^3$ is the number of total atoms in the nanomaterials. We can rewrite the relation (2) as follows:

$$E_c(r) = E_c(\infty) \left[1 - 6\gamma \frac{r}{2R} \right] \quad (3)$$

where $E_c(\infty) = n\beta E_{bond} / 2$ and γ is the shape factor, which is defined as the ratio of surface area of the particle in any shape to the surface area of spherical nanoparticle for the same volume. Apparently, the shape factor equals unity for spherical shapes and larger than for non spherical shapes. It should be mentioned that the shape factor is just a familiar parameter, by which the properties of non spherical nanosolids can be labeled roughly from the results given by spherical nanosolids.

In terms of diameter of nanomaterial (D) and the diameter of an atom (d), equation (3) may be rewritten as

$$E_c(D) = E_c(\infty) \left[1 - 3\gamma \frac{d}{D} \right] \quad (4)$$

The lattice constants [14] can be calculated for different structures like body centered structure, face centered structure and hexagonal closed packed structure as follow:

$$d = \begin{cases} \left(\frac{3a^3}{\pi} \right)^{1/3} \\ \left(\frac{3a^3}{2\pi} \right)^{1/3} \\ \left(\frac{3\sqrt{3}a^2 c}{2\pi} \right)^{1/3} \end{cases} \quad (5)$$

Melting temperature is the parameter to estimate the strength of metallic bonds. On the basis of Lindemann's [15] criterion of melting, the melting temperature is linear to the force constant of the lattice vibration, which can be expressed by the cohesive energy. Meaning that, the cohesive energy of the solids and melting temperature are linearly related. In line with the relationship (4) the melting temperature for nanosolids is given as

$$T_m(D) = T_m(\infty) \left[1 - 3\gamma \frac{d}{D} \right] \quad (6)$$

where $T_m(D)$ and $T_m(\infty)$ are melting temperature for nanosolids and its bulk counterparts.

The force between the atoms is reflected in the Debye temperature and it is useful to have this as a reference to characterize a crystal. The Debye temperature is a measure of the vibrational response of the material. One may get the connection between the melting point and the Debye temperature [16]. According to this, the relation between Debye temperature and melting temperature is given as

$$\theta_{Debye}^{\ 2} \propto \left(\frac{T_m}{MV^{2/3}} \right) \quad (7)$$

where M is the molecular mass and V is the molar volume. Thus, from equations (6) and (7), we get the relation of Debye temperature as

$$\theta_{Debye}(D) = \theta_{Debye}(\infty) \sqrt{1 - 3\gamma \frac{d}{D}}$$

On binomial expansion and ignoring the higher order terms as their contributions become less and less, we get

$$\theta_{Debye}(D) = \theta_{Debye}(\infty) \left[1 - \frac{3}{2} \frac{\gamma d}{D} - \frac{9}{8} \frac{\gamma^2 d^2}{D^2} - \frac{27}{16} \frac{\gamma^3 d^3}{D^3} \right] \quad (8)$$

Where $\theta_{Debye}(D)$ and $\theta_{Debye}(\infty)$ are Debye temperature for nanosolids and its bulk counterparts. Equations (6) and (8) are the more general relations for the size and shape dependent melting temperature and Debye temperature of nanosolids respectively.

Table 1: Input Parameters [2] Used to Determine $T_m(D)$ and $\theta_{Debye}(D)$

Nano solids	d(nm)	Tm (∞) [K]	$\theta_{Debye}(\infty)$ [K]
Se	0.230	494	135.5
In	0.319	429.8	129
Co	0.251	1768	359

3. Results and discussion

Based on bond energy theory, the size and shape dependent melting temperature and Debye temperature are studied for the Se, In and Co nanosolids. Input parameters [2] used in the computation in equations (6) and (8) are listed in Table 1. The Variation of melting temperature and Debye temperature of these nanosolids has been discussed and their graphical representation of the calculated results is shown in Figs. 1-6, along with available experimental findings. It is seen that the melting temperature and the Debye temperature decrease with the decreasing in size, which exhibits that the strength of the metallic bond of nanosolids is weaker than that of corresponding bulk solids. To account for the shape of the cross section, shape factor $\gamma =$ 1, 1.18, 1.24 and 1.49 in spherical, octahedral, hexahedral and tetrahedral shapes is incorporated and it is clearly confirmed by this study that melting temperature and Debye temperature are not only a size dependent but also depends upon the shape. For the comparison purpose we have plotted the spherical, octahedral, hexahedral and tetrahedral shapes nanosolid on the same figures. It is observed that the effect of size increases as we go $\gamma =$ 1, 1.18, 1.24 and 1.49 of spherical, octahedral, hexahedral and tetrahedral shapes. It is reported that at a particular size, the melting temperature and the Debye temperature is maximum for spherical shape and minimum for tetragonal shape. This behaviour can be explained, as the particle size reduces, surface to volume ratio of the nanosolids increases. Therefore, the number of dangling bonds increases, as a result the melting temperature and the Debye temperature decrease with decreasing the particle size. Since, the melting temperature is a parameter to evaluate the strength of metallic bond. Therefore, the melting temperature variations of Se, In and Co are calculated by (6) and are reported in Figs. 1-3 along with the available experimental data [17]. The melting temperatures are computed for the sizes ranging from [2] nm to 30 nm. The depression of melting temperature is dramatic in the lower range of size while it becomes smoothly in large size. When the particle size is very small, the surface volume atomic ratio increases as the surface area increases. Indeed, for a particle with diameter around 10nm, the surface atoms occupy nearly one quarter of the total number of atoms and effects the physical properties of the nanosolids. From Figs. 1-3, it can be seen that the reduction of melting temperature is appreciable in the sizes ranging from 2 to 8 nm. When the particle size is

above the 15 nm, there is a slightly decrease the value of melting temperature. It may be concluded that the melting temperature of the nanosolids decreases as the size decreases and the effect is more when the shape factor varies from 1 to 1.49. It is shown by (8) that the Debye temperature is the function of shape factor (γ) and the particle size (D). The variation of the Debye temperature with size and shape are reported and shown in Figs. 4-6, along with the available experimental data [18, 19] for comparison purpose. From Figs. 4-6, it is observed that the Debye temperature decreases with decreasing size and increasing the shape factor. It can be realized that the size effect on Debye temperature are dominant in the sizes ranging from [2] nm to 10 nm. When the size is beyond to 15 nm the variations are too small to be ignored. The decreased nature of the Debye temperature can be explained on the basis of the surface volume ratio and the weakness of the metal-metal bonds compared with its bulk counterpart. Moreover, the surface area increases with the increase of the shape factor. Thus, the surface effect on the Debye temperature of nanosolids might be supported in the large shape factor, which suggests to the decreasing of the Debye temperature. Moreover, during the melting process, the thermal expansion exists due to the electron phonon anharmonic interaction; consequently, the shape factor may be practical to define the shape dependent lattice expansion also.

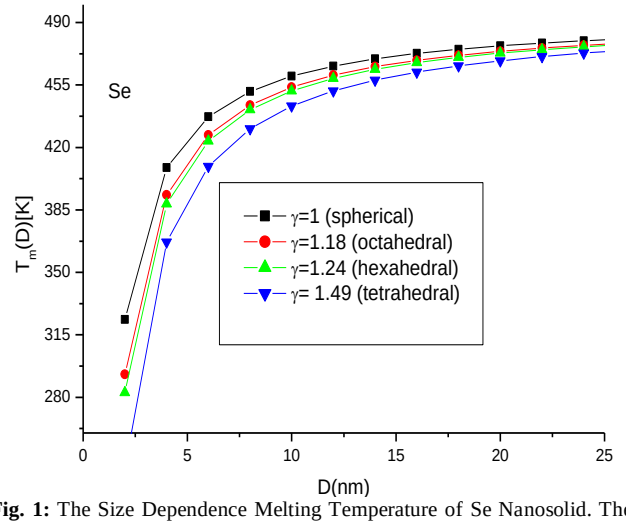

Fig. 1: The Size Dependence Melting Temperature of Se Nanosolid. The Solid Lines with Symbols Corrospond to (6) with Shape Factor γ = 1, 1.18, 1.24 and 1.49.

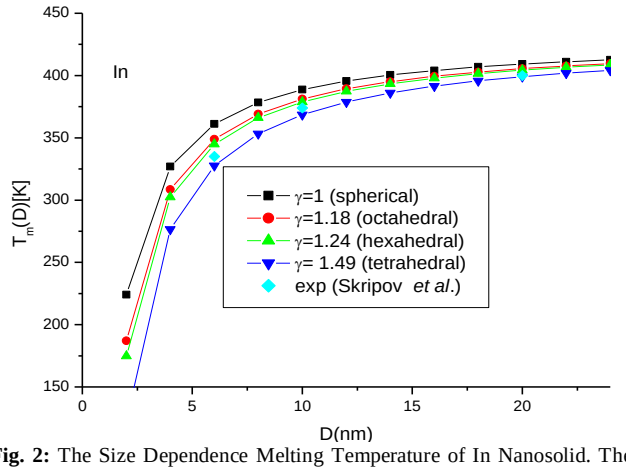

Fig. 2: The Size Dependence Melting Temperature of In Nanosolid. The Solid Lines with Symbols Corrospond to (6) with Shape Factor γ = 1, 1.18, 1.24 and 1.49 and the Symbols ♦ Denote the Experimental Values of In Nanosolids [17].

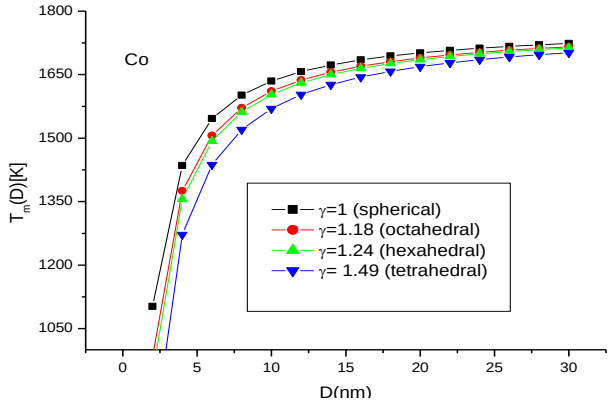

Fig. 3: The Size Dependence Melting Temperature of Co Nanosolid. The Solid Lines with Symbols Corrospond to (6) with Shape Factor γ = 1, 1.18, 1.24 and 1.49.

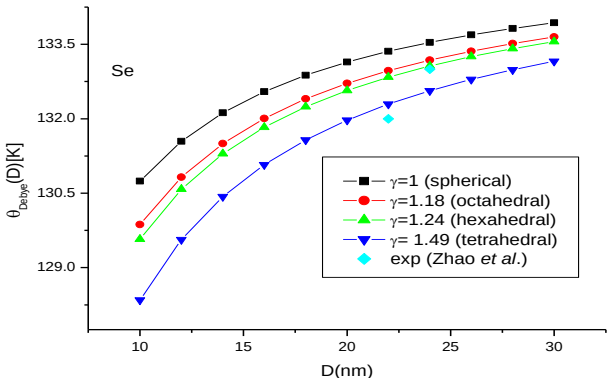

Fig. 4: The Size Dependence Debye Temperature of Se Nanosolid. The Solid Lines with Symbols Corrospond to (8) with Shape Factor γ = 1, 1.18, 1.24 and 1.49 and the Symbols ♦ Denote the Experimental Values of Se Nanosolids [18].

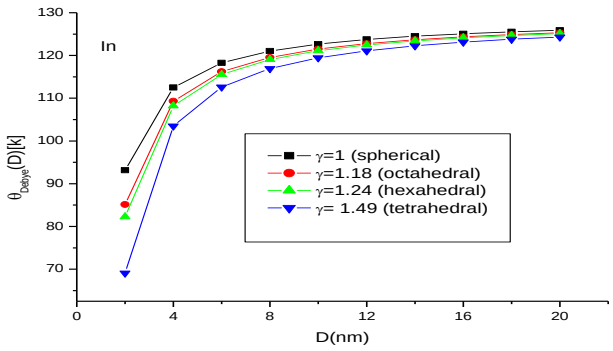

Fig. 5: The Size Dependence Debye Temperature of In Nanosolid. the Solid Lines with Symbols Corrospond to (8) with Shape Factor γ = 1, 1.18, 1.24 and 1.49.

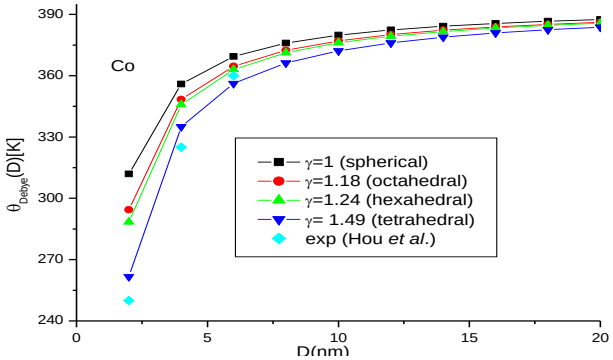

Fig. 6: The Size Dependence Debye Temperature of Co Nanosolid. The Solid Lines with Symbols Corrospond to (8) with Shape Factor γ = 1, 1.18, 1.24 and 1.49 and the Symbols ♦ Denote the Experimental Values of Co Nanosolids [19].

4. Conclusion

The surface free energy model has been extended to calculate the size and shape dependent thermodynamical properties of the nanosolids. We have studied the melting temperature and Debye temperature in different sizes and shapes of Se, In and Co nanosolids. It is observed that the computed results of melting temperature and Debye temperature decrease with deceasing size of these nanosolids. The explanations lie in the interatomic interaction and increased surface to volume ratio. Also, it is realized that the particle shape affects the melting temperature and Debye temperature of the nanomaterials. The effect becomes more with the reducing of particle size. The method studied in this paper might have viable application to find the size and shape dependent melting temperature and Debye temperature of nanosolids where experimental data do not exist.

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