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Effect of Size dependent thermodynamic properties of Transition Nano metals

1. Abhishek Gautam
2. Dharam Veer Singh

Dr. B.R. Ambedkar University- Agra (U.P.), India

Received-08.04.2023, Revised-14.04.2023, Accepted-19.04.2023 E-mail: peetambrask@gmail.com

Abstract: ***Even today, it is extremely difficult to describe and understand thermophysical phenomena at the nanoscale. In order to examine the effects of size on thermodynamic parameters, such as melting temperature, Debye temperature, and specific heat capacity of nanoparticles, surface effect led to the formulation of a theoretical model. In order to relate the ratio of a nanomaterial's surface area to volume and its size-dependent thermodynamic properties, cohesive energy, a thermodynamic parameter, was used. Due to their prospective uses in research and technology, the nanoparticles Au, Ag, Cu, and 7Se were chosen for examination in this contribution. It was discovered that as size is reduced up to critical sizes, the melting temperature, Debye temperature, and specific heat capacity of nanoscale size materials fall. On the other hand, as the size of the nanoparticles is reduced, the specific heat capacity tends to increase. When the current findings for melting temperature and Debye temperature are compared to theoretical and experimental measurements, sufficient agreements are found.***

Key Words: : Nanoparticle, melting temperature, Debye temperature, specific heat, contribution, modynamic.

Researchers have discovered a brand-new field of study called "Nanoscience & Nanotechnology" over the past two decades, and it has fundamentally altered how we think about the physical phenomena that occur at tiny dimensions of materials. Researchers paid particular attention to this newly growing field. This field of study is highly broad and interdisciplinary, and it has important applications in business and the medical sciences. Due to the high size and shape dependence of materials at the nano level, the fields of nanoscience and nanotechnology are very fascinating and exciting. Unfortunately, the conventional theories utilized for the materials at their bulk counterparts cannot adequately describe and explain it[1-7]. The huge surface to volume ratio and maybe a change in the material's structure are to blame for the unexpected behavior of materials at the nanoscale [8].

An inductive line of physics research has developed around the investigation of nanomaterial behaviour. Structure affects the physical and chemical characteristics of bulk materials. Although the features of nanomaterials are not solely influenced by their structure, their size and shape are frequently the most important ones. [9,10]. The number of atoms that make up a single particle is a crucial factor in establishing the crystal structure and the energy of a material's states [3]. The majority of a material's atoms occupy the surface when it is in the nanoscale size range, increasing the surface area. This element can change a variety of intriguing physical characteristics. For instance, particle size is related to phonon density of state shift by M.S.[11], an increase in elastic modulus of nanoparticles, and a decrease in melting temperature in nanomaterials[9,12].

Melting entropy is the difference between the lattice points and the state of order of melting. Behaviors of crystalline solids such bulk modulus, thermal expansion, melting point, and structural change are all heavily influenced by melting entropy, according to J.S. [13]. Thus, for a better comprehension of the thermodynamic properties of nanomaterials, The majority of the thermodynamic properties of nanomaterials, such as the Debye temperature, melting point, and heat conductivity, drop as the size of the material decreases. On the other hand, when a nanomaterial's size is reduced, the specific heat increases[14]. Because the nanomaterial has a large percentage of surface atoms that are loosely bound to the inside atoms, the melting point decreases as the size of the nanoparticles increases. Experiments [15, 16] have supported the hypothesis that the thermodynamic properties vary with size. Experimental research has been done to determine the melting point of Au, Ag, Cu, and Se nanoparticles with diameters between 1 and 25 nm[17]. Omar, M.S. [11] has thoroughly researched these phenomenon. Additionally, Qi[3] provided a methodology, analogous to equation (4), for figuring out the melting point of nanomaterial. This model takes into account a form factor as a significant parameter for defining the melting point's size dependency. Different particle forms were considered, and it was found that melting temperatures varied depending on the shape factor and at various sizes. The impact of changing size on the lattice parameter has been the subject of numerous investigations. The relationship between the lattice parameter of nanoparticles and particle size has been demonstrated by experimental and theoretical studies[11, 12, 24]. Omer[11] presented a model to explain how size affects the mean bond length in nanomaterials and created a formula to show how the lattice parameter and lattice volume are affected by size. As a result, the relative lattice volume has varied along with the melting point of nanoscale particles and has decreased as particle

Corresponding Author / Joint Authors

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Vol.-16, No.- II, Issues-28, YEAR- April-June-2023

sizes have increased. On the other hand, as nanomaterial size increases, the specific heat increases. In order to establish a formula for the effect of size on bulk modulus, the variation of relative lattice volume was combined with the melting point of nanoscale particles[13]. Qi[1] also proposed that the lattice parameter contracts for isolated nanoparticles and derived an expression for the variation of lattice parameter with size and shape. Qi[1] further assumed that if a particle is taken out from bulk material having the same structure to form a nanoparticle, one can visualize that the particle would have the same structure as that of its bulk counterpart. Thus, the lattice volume of nanomaterials is reduced as a result of the contraction of the lattice parameter. The fraction of volume contraction of Al, Au, and Ag nanoparticles was calculated by Sadaiyandi[14] using the Qi[1] model. To create equations for the size dependence of melting point, Debye temperature, melting entropy, and heat capacity in the current work, the relationship between cohesive energy and melting point was taken into consideration. This study will focus on how Si and Au's aforementioned thermodynamic properties vary. As a first approximation, it has been discovered that the majority of the thermodynamic behavior of nanoparticles varies according to the inverse of the nanoparticle diameter, with the exception of the specific heat capacity, which rises with decreasing particle size. The figures are supplemented with experimental and theoretical published data for comparison, and acceptable consistency is seen.

THEORY AND DISCUSSION

1. Melting temperature- The melting point of nanoparticles has been discovered to be much lower than that of bulk materials. In order to examine the behavior of melting entropy of nanomaterial, researchers have investigated a number of different thermodynamic models [13,15]. The cohesive energy, which is responsible for determining the majority of the thermodynamic properties of materials [16], is an essential thermodynamic parameter for deriving a size dependent formula of melting point. The cohesive energy of a nanomaterial is the sum of the contribution of the surface atoms and the atoms in the interior, which can be written as [1]:

$$E_{tot} = E_0 (n - N) + \frac{1}{2} E_0 N \quad \ldots(1)$$

Where, Eo is the cohesive energy of an atom, n is the number of atoms comprising the material and N is the number of atoms occupied the surface. (n-N) is the number of interior atoms. Eq. (1) is rewritten to express the energy per a mole

$$\frac{AE_{tot}}{n} = AE_0 \left(1 - \frac{N}{n}\right) + \frac{1}{2n} AE_0 N \quad \ldots(2)$$

A is the Avogadro's number.

AE total /n = En is the cohesive energy per a mole of the nanomaterial.

AEo = Eb is the cohesive energy per mole of bulk material.

Eq. (2) is arranged to form En:

$$E_n = E_b \left(1 - \frac{N}{2n}\right) \quad \ldots(3)$$

The cohesive energy is proposed to be linearly related to the melting temperature [23] therefore, the relation for nanomaterials melting temperature Tn is formulated by the following

$$Tn = T_b \left(1 - \frac{N}{2n}\right) \quad \ldots(4)$$

Where, Tb is the melting point of the bulk state which is constant. N/2n depends on the size and shape of the nanomaterials. For nanoparticles N/2n = 2d/D, d is the atomic diameter and D diameter of the considered nanoparticle [1]. Therefore, from Eq. (4), the size dependence of T_n is expressed as:

$$T_n = T_b \left(1 - \frac{2d}{D}\right) \quad \ldots(5)$$

Eq.(5) indicates that melting temperature (Tn) varies with the inverse of the diameter (D-1) of the nanoparticle, while d is the atomic diameter and depends on the structure of the material and it is size independent. Xiong [15] used Gibbs free energy for surface and bulk atoms to formulate an equation analogue to Eq. (5)

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e-ISSN NO.-2582-2454 (Online)
Vol.-16, No.- II, Issues-28, YEAR- April-June-2023

2. Debye temperature- The Debye temperatureqθ_D is an important thermodynamic quantity, which appears in Debye theory of specific heat capacity of solid. Debye temperature is defined mathematically as:

$$\theta_D = \frac{h\omega D}{K_B} \quad \ldots(6)$$

Where $w_D$is the Debye frequency and $K_B$is Boltzmann constant.

For nanomaterials, the amplitude of the vibration of the surface atoms is higher than that of the bulk atoms and their vibrational frequencies is smaller in comparison with that of the bulk material [4,17]. Hence, Eq. (6) predicts that θ_D for nanomaterials decreases as the size is reduced. Lindemann's melting theory states that crystals melt when the root mean square displacement of atoms become greater than some fractions of the interatomic spaces in the solid, which can also be valid for nanoparticles. Hence, melting temperature $T_b$and Debye temperature θ_Db for bulk materials are combined as [18]

$$\theta_{Db}\alpha\left(\frac{T_b}{MV^2/3}\right)1/2 \quad \ldots(7)$$

Where, Tb is the melting point of bulk state, M is the molecular mass, and V is the lattice volume per atom. Similarly nanomaterial Debye temperature $Q_{Dn}$is

$$\theta_{Dn} \propto(\frac{T_n}{MV^2/_3})\ ^1/_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Dividing Eq. (8) by Eq. (7) a relationship for θ_Dn is obtained:

$$\frac{\theta_{D_n}}{\theta_{D_b}} = \ (\frac{T_n}{T_b})\ ^1/_29)$$

$T_b$is constant for an assumed material. From Eq. (5) θ_Dn is given as a function of particle diameter

$$\theta_{D_n} = \theta_{Db}\left(1-\frac{2d}{D}\right)1/2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

Eq. (10) is used in the current study to evaluate the size dependent θ_Dn for Si and Au nanoparticles.

2. Specific heat capacity- An important thermodynamic quantity which is expected to vary under the influence of changing size of nanomaterials is the heat capacity. Specific heat is the amount of energy supplied to rise the temperature of a unit mass of a material by one degree of, the specific heat capacity of a material depends only on temperature. However, due to the surface effect, the specific heat of nanomaterials. Many experimental and theoretical studies have been performed to investigate the effect of size on specific heat This implies that in the range of nanoscale size the specific heat capacity varies with both temperature and size. A relationship between specific heat of bulk material C_{pb} and Debye temperature at constant pressure is obtained, on the basis of Debye's theory

$$C_{pb} \propto \frac{1}{\theta^2_{Db}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

Similarly, for nanomaterials, the expression is:

$$C_{pb} \propto \frac{1}{\theta^2_{Dn}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

Eq. (11) is divided by Eq. (12) to get this form:

$$C_{pn} = C_{pb}\,(\frac{\theta_{Dn}}{\theta_{Db}})^{-\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

ISSN NO.-2347-2944 (Print)
e-ISSN NO.-2582-2454 (Online)
Vol.-16, No.- II, Issues-28, YEAR- April-June-2023

is the specific heat of nanomaterial. Substituting Eq. (10) in to Eq. (13), The size dependence of C_{pn} is obtained in the following relation:

$$C_{pn} = C_{pb}\left(1 - \frac{2d}{D}\right)^{\frac{-1}{}} \qquad (14)$$

Eq. (14) represents the nanomaterial specific heat in terms of its bulk specific heat and as a function of size. For nanomaterials, C_{pn} is predicted to rise with decreasing size. Theenhancement in specific heat at small sizes is caused by a high contribution of the surface atoms

Table 1. The Calculated values of Au-nanopatical melting Temperature

Au	**Melting temperature(T_m)**	
Size (nm)	**Experimental values (k)**	**Theoretical values** (Calculated) **(k)**
05	1000	995
10	1180	1166
15	1250	1222
20	1280	1250
25	1360	1267
30	1366	1279

Table 2. The Calculated values of Au-nanopatical debar temperature.

Au	**Debay temperature(Q_D)**	
Size (nm)	**Experimental values (k)**	**Theoretical values** (Calculated) **(k)**
05	90	158
10	105	171.65
15	120	176,15
20	135	178.13
25	150	179.244
30	158	177.72

Table 3. The Calculated values of Au-nanopatical specific heat capacity.

Au	**Specific heat capacity (c_{pn})**	
Size (nm)	**Experimental values (k)**	**Theoretical values** (Calculated) **(k)**
05	155	173.18
10	142	147.86
15	140	140.78
20	139	137.78
25	125	135.93
30	126	134.12

Table 4. The Calculated values of Ag- nanopatical melting temperature

Ag	**Melting temperature(T_m)**	
Size (nm)	**Experimental values (k)**	**Theoretical values** (Calculated) **(k)**
05	700	655
10	890	807
15	900	858

Table 5. The Calculated values of Ag –nanopatical debay temperature.

Ag	**Debay temperature(Q_D)**	
Size (nm)	**Experimental values (k)**	**Theoretical values** (Calculated) **(k)**
05	180	185.85
10	200	206.34
15	205	212.73
20	208	215
25	210	217.71
30	215	218

ISSN NO.-2347-2944 (Print)
e-ISSN NO.-2582-2454 (Online)
Vol.-16, No.- II, Issues-28, YEAR- April-June-2023

Table 6. The Calculated values of Ag _ nanopatical specific heat capacity

Ag	Specific heat capacity (c_{pn})	
Size (nm)	Experimental values (k)	Theoretical values (Calculated) (k)
05	354	344.37
10	319	279.36
15	316	263.83
20	312	255
25	309	250
30	294	248.13

Table 7. The Calculated values of Cu nanopatical melting memperature

Cu	Melting temperature(T_m)	
Size (nm)	Experimental values (k)	Theoretical values (Calculated) (k)
05	890	861.99
10	1020	972.89
15	1050	1009.96
20	1100	1028
25	1200	1039.59
30	1202	1062.92

Table 8. The Calculated values of Cu –nanopatical debay temperature

Cu	DebayTemperature(Q_D)	
Size (nm)	Experimental values (k)	Theoretical values (Calculated) (k)
05	600	305.85
10	750	324.95
15	900	331.06
20	1005	334.08
25	1220	335.86
30	1222	349

Table 9. The Calculated values of Cu-nanopatical specific heat capacity.

Cu	Specific heat capacity (c_{pn})	
Size (nm)	Experimental values (k)	Theoretical values (Calculated) (k)
05	414	486.67
10	354	431.35
15	318	407.92
20	306	403.52
25	300	402.7
30	298	400.5

Table 10. The Calculated values of Se-nanopatical melting temperature

Se	Melting temperature(T_m)	
Size (nm)	Experimental values (k)	Theoretical values (Calculated) (k)
05	354	438
10	324	466
15	322	493
20	318	480
25	317	482
30	318	484.77

Table 11. The Calculated values of Se –nanopatical debay temperature.

Se	Debay temperature(Q_D)	
Size (nm)	Experimental values (k)	Theoretical values (Calculated) (k)
05	128	127
10	129	131
15	130	132
20	133.4	133
25	133.6	133
30	134	133.73

ISSN NO.-2347-2944 (Print)
e-ISSN NO.-2582-2454 (Online)
Vol.-16, No.- II, Issues-28, YEAR- April-June-2023

Table 12. The Calculated values of Se-nanopatical specific heat capacity.

Se	Specific heat capacity (c_{pn})	
Size (nm)	Experimental values (k)	Theoretical values (Calculated) (k)
05	354	359
10	324	337
15	322	330
20	318	328
25	317	326
30	321	325.35

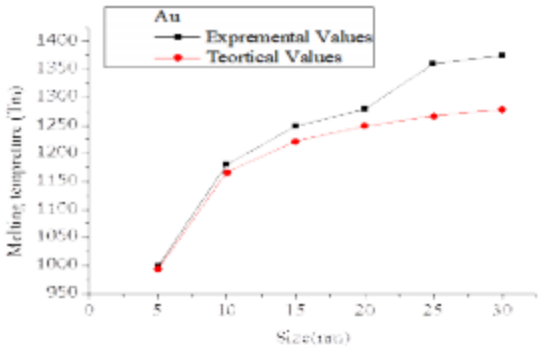

Figure 1. Size different calculated melting temperature

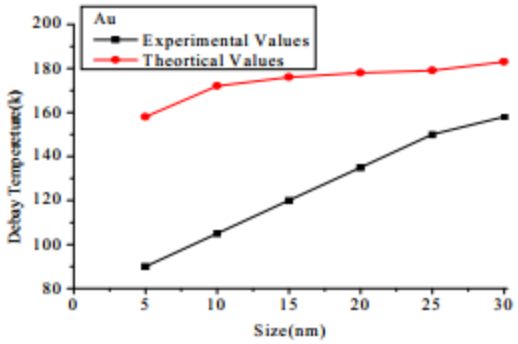

Figure 2. Size different calculated debay temperature

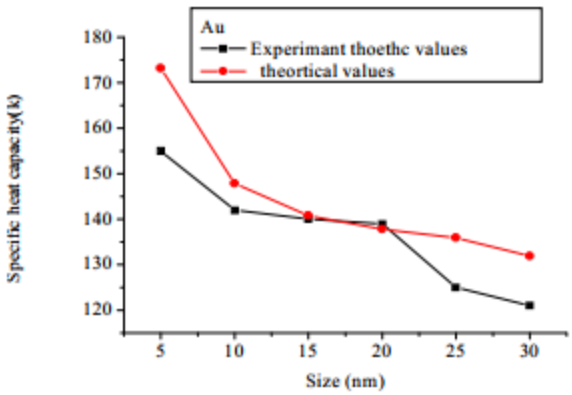

Figure 3. Size different calculated Specific heat capacity

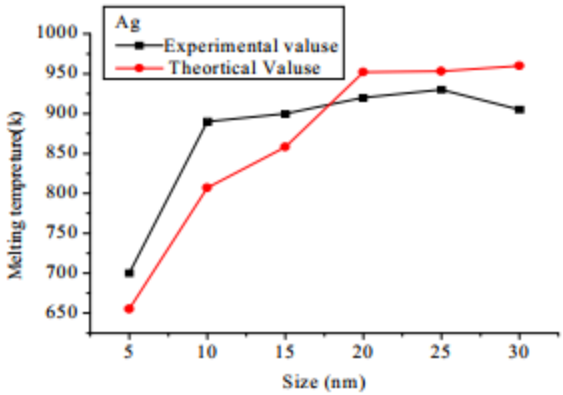

Figure 4. Size different calculated Melting tempreture

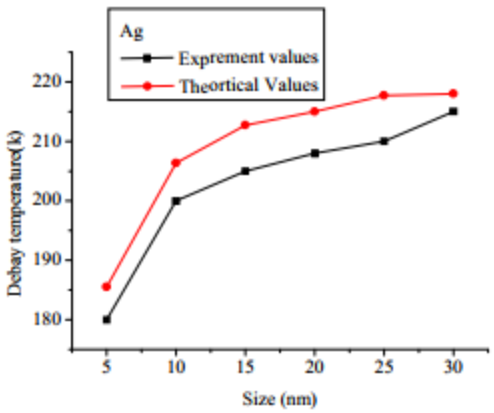

Figure 5 Size different calculated debay temperature

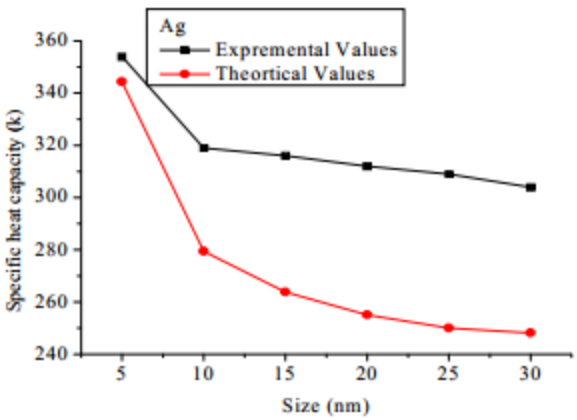

Figure 6. Size different calculated Specific heat capacity

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Vol.-16, No.- II, Issues-28, YEAR- April-June-2023

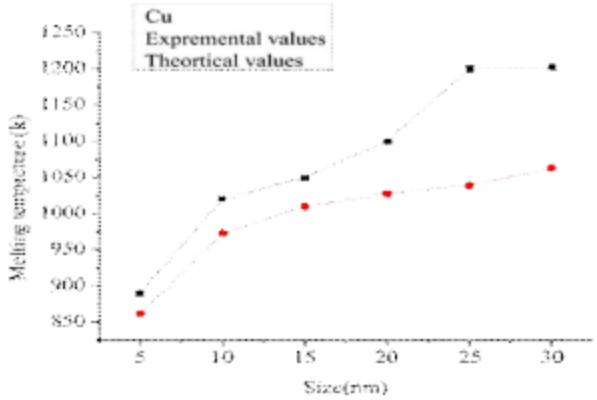

Figure 7 Size different calculated Melting tempreture

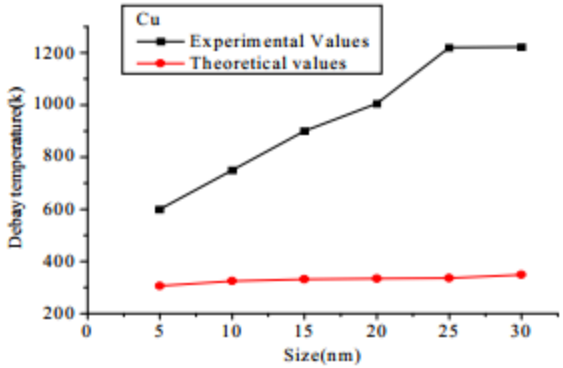

Figure 8 Size different calculated debay temperature

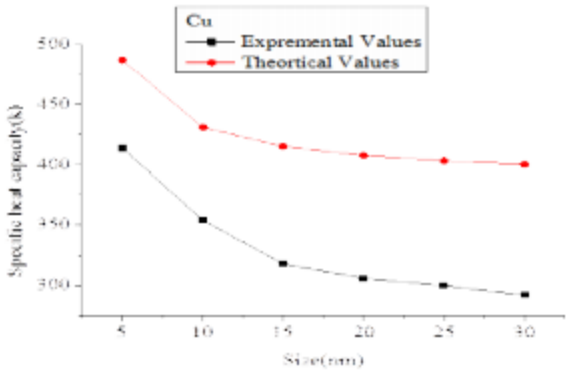

Figure 9. Size different calculated Specific heat capacity

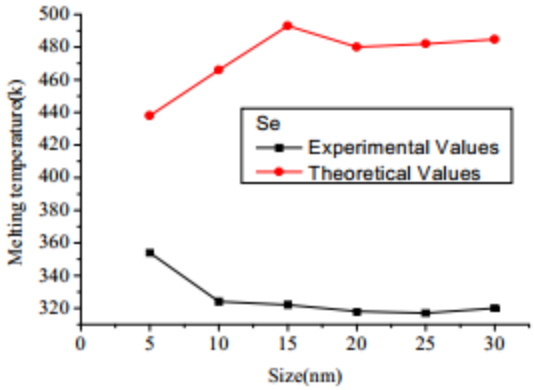

Figure 10. Size different calculated melting temperature

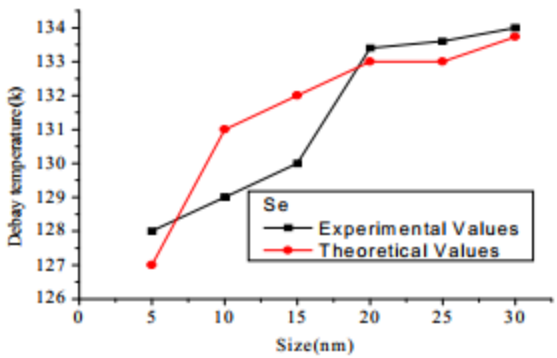

Figure 11. Size different calculated debay temperature

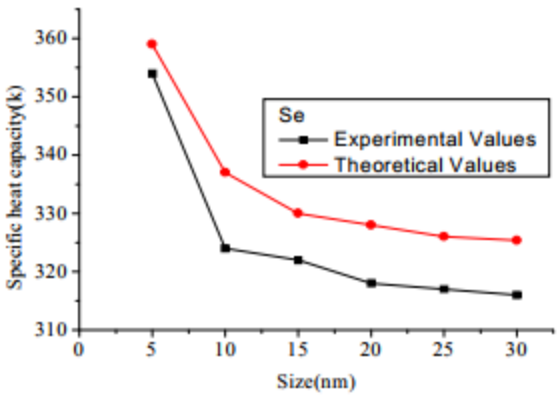

Figure 12. Size different calculated specific heat capacity

RESULTS AND DISCUSSION- The required parameters in this study are presented in Table[1-12] The important thermodynamic properties of nanoscale materials, such as melting point Tn, Debye temperature ?_Dn and specific heat capacity Cpn for Au, Ag, Cu, Se have been studied. Eq. (5) was used to evaluate the variation of melting point with decreasing the diameter D of nanoparticles. Figures 1,2,3,4 indicates that melting temperature for Au, Ag, Cu, Se nanoparticle drops with the decrease the in the size of the nanoparticle. From the melting curves, two main trends can be observed. For diameters D larger than 5nm, melting temperature decreases steadily with altering size and the curves are appeared nearly invariant. However, in contrast, the effect of size is very different where D <10 Melting temperature drops rapidly with a slight decrease in the particle size below the limit of 10nm. For both considered nanoparticles, when the diameter is reduced to around 5nm the trend of melting temperature declines to about half of the bulk value The present results of melting Temperature of, Au Ag, Cu, Se have been compared with experimental and theoretical data, and substantial agreements can be observed with all results.

ISSN NO.-2347-2944 (Print)
e-ISSN NO.-2582-2454 (Online)
Vol.-16, No.- II, Issues-28, YEAR- April-June-2023

Regarding to Tn values of Au, Ag, Cu, Se nanoparticle in the Figure1, 2,3,4, a better accord with experimental data. Figures[1-4] represent the results of size dependence of Debye temperature ?_Dn for Au,Ag,Cu,Senanoparticles calculated using Eq. (10). It is observed that the ?_Dn reduces non-linearly with the decrease in the diameter of the particles. One can find that the ?_Dn alters very slowly with the particle's dimension when values of the diameter D are greater than 10nm. After this limit, Debye temperature drops sharply for Au ,Ag, Cu. Se nanoparticles considered to study. This trend is attributed that as the nanoparticles size decreases the frequency of vibrations drops and Debye temperature varies with Debye frequency [25, 26]. The present results of Debye Temperature of Au, Ag, Cu, Se have been compared with experimental and theoretical data, and substantial agreements can be observed with all results. Regarding to ?_Dn values of Au ,Ag, Cu, Se nanoparticle in the Figure[1,4 ,3] a better accord with experimental data.

Further interesting investigation, is the understanding of specific heat capacity dependence on nanoparticle size. Apart from the above studied thermodynamic quantities, it is expected from Eq.[14], that as the size of the nonmaterial is decreased the specific heat capacity Cpn tends to increase. Figure [1-4]shows how the Cpn of Au, Ag, Cu, Se nanoparticle increases with the reduction in their diameters. It is shown that Cpn increases very slightly when the size decreases from 30nm to 10 nm. While, as the size decreased further from 10nm towards 0nm, the curves of the specific heat rose dramatically to around double value of that of the bulk state. Specific heat of nonmaterial is found to depend on lattice vibrations [30]. There are two vibrations contribute to the specific heat capacity of nonmaterials, the interior atom vibrations and an additional surface atom vibrations[31]. The present results of specific heat capacity of Au, Ag, Cu, Se have been compared with experimental and theoretical data, and substantial agreements can be observed with all results. Regarding to Cpn values of Au, Ag, Cu, Se nanoparticle in the Figure [9 ,10,11,12] a better accord with experimental data.

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