International Journal of Nanotechnology and Applications
ISSN 0973-631X Volume 11, Number 1 (2017), pp. 81-90

http://www.ripublication.com

Prediction for the Debye Temperature of Metallic Nanoparticles

Brijesh K Pandey[1*] and Ratan L Jaiswal[2]

[1]Deptt. of Applied Science, MMM University of Technology, Gorakhpur (UP), India.

[2]Deptt. of Physics, SSSVS Govt. P.G. College, Chunar Mirzapur (UP), India

Abstract

Predictions for the variation of physical properties of nanomaterials have been a matter of great debate in the recent decades. Different researchers have reported drastic change in the physical properties of metals at their nano scale. In the present work, we have studied the Debye temperature of spherical nanosolid, nanowire and nanofilms of Aluminium (Al), Copper (Cu), Paladium (Pd) and Platinum (Pt) having their sizes less than 30 nm. For computation we have consider the fundamental relation of cohesive energy with melting point. During our study it is found that there is a drastic change in the Debye temperature of spherical nanosolid, nanowire and nanofilms of metals below 20 nm. In this variation,it is also observed that there is maximum variation of Debye temperature is in case of nanofilms while minimum in case of spherical nanosolids and moderate change in case of nanowires. Variation in Debye temperature has been interpreted on the basis of the presence of number of surface atoms due to the change in surface to volume ratio of metals at the nano level. We have compared our computed results with the available experimental data which shows their good agreement.

Keywords: Metallic nanoparticles, Debye temperature and Metallic nanostructure materials.

1. INTRODUCTION:

In the nanoscience and nanotechnology, the size of materials has reduced at the very low scale nanometer at least one dimension. In this size range, the surface to volume ratio is much increased and correspondingly the physical, chemical, and mechanical properties are changed[1-3]. The properties of material at nanoscale are different from

the corresponding bulk material. The property of nanomaterials change drastically as the size reduces below 30 nanometers.A sample of gold appears red at 10 nanometers. Its melting temperature decreases rapidly as their sizesare reduced up to the level of nano scale [4-5].

Our purpose is to determine the Debye temperatureof the nanomaterials which is closely related to the cohesive energy of the nanomaterials. The cohesive energy or heat of sublimation is an important physical quantity to account for the strength of metallic bonds. The cohesive energy is the energy to divide the metallic crystal into individual atoms. For the above said purpose we studied the equation of state for the size dependent Debye temperature of the nanoparticles of metals Aluminium (Al), Copper (Cu), Paladium (Pd) and Platinum (Pt). We have computed the Debye temperature of spherical nanosolid, nanowire and nanofilm of the considered samples. With the different mode of variation, it is observed that the Debye temperature of metals at nano levelincreases with increase of theirsizes.

2. METHOD OF ANALYSIS :

The total cohesive energy of the nano crystalline solid, is given by

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

Equation (1) is the sum of energy due to the contribution of the interior atoms as well as the surface atoms of nanocrystalline solids. Here E_0 is the cohesive energy of the bulk materials per atom, n is the total no of atoms of nanosolid and N is the number of atoms at surface. [6]

For the cohesive energy per mole, the equation (1) may be written as

$$A_vE_{tot} = E_0A_v\,(n-N) + \frac{1}{2}A_vE_oN$$

$$\frac{A_vE_{tot}}{n} = E_0A_v\left(1-\frac{N}{n}\right) + \frac{A_vE_0\,N}{2n} \ldots (2)$$

Where,A_v is Avagadro number. The term $\frac{A_vE_{tot}}{n} = E_n$represents the cohesive energy per mole of the nanocrystalline solid and $E_0A_v = E_b$ is the cohesive energy per mole of the corresponding bulk material.

Thus equation (2) becomes,

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

Since the cohesive energy is linearly related to the melting temperature,[7-8], therefore the melting temperature of the nanosolid can be written as

$$T_{mn} = T_{mb}(1-\frac{N}{2n}) \ldots (4)$$

According Lindermann criterion, a crystal melts when the root mean square displacement of atoms in the crystal exceeds a certain of the interatomic distance in the crystal[9]. The Debye temperatureθ_D is related with melting temperature as,

$$\theta_D = constt.\left(\frac{T_m}{MV^{2/3}}\right)^{1/2} \quad \ldots\ldots (5)$$

Where M is the molecular mass and V is the volume per atom.

If $\theta_{Dn}$and θ_{Db} represent the Debye temperature of material of nano sized and of bulk material respectively, we can write,

$$\frac{\theta_{Dn}}{\theta_{Db}} = \left(\frac{T_{mn}}{T_{mb}}\right)^{1/2} \quad \ldots\ldots.. (6)$$

$$\frac{\theta_{Dn}}{\theta_{Db}} = \left(1 - \frac{N}{2n}\right)^{1/2} \quad \ldots\ldots (7)$$

The value of $\left(\frac{N}{2n}\right)$ depends upon the structure of the nanomaterial and has been calculated for different shape of nanomaterials [5].

For spherical nanosolids, $\frac{N}{2n} = \frac{2d}{D}$ …….(8)

Where, D and dare the diameters of spherical nanosolid and that for atom respectively.

For nanowires, $\frac{N}{2n} = \frac{4d}{3L}$ …….(9)

Where, L is diameter of nanowire.

And for nanofilm, $\frac{N}{2n} = \frac{2d}{3h}$ …….(10)

Where h is height of nanofilm.

Table: 1: Input Parameters of Eq. (4) and Eq. (7)

Metals	Atomic Diameter, d (nm) .[11]
Copper (Cu)	0.2822
Palladium (Pd)	0.3040
Platinum(Pt)	0.3064
Aluminum (Al)	0.3165

3. RESULT AND DISCUSSION

In our present work we have studied the variation of melting and Debye temperature of nanocrystalline metals given in the table-1. To compute the melting temperature of nanocrystalline copper, palladium, platinum and aluminum equation (4) is used in which the required input data has been taken from table-1 [3]. The computed values of melting point (temperature) of Cu, Pd, Pt and Al (nanosolid, nanowire and nanofilm) are plotted against the size of corresponding nanostructuresgiven in Fig.(1) – Fig.(4) along with available experimental data[10]. During our study of size dependence of melting temperature, it is found that melting temperature of metal nanostructures decreases in the small range of their sizes (10-20nm) after that it becomes almost constant. The melting curves can be divided into two parts, sizes larger than 10 nm and sizes less than 10 nm. Melting temperature changes gently with the variation of size and the curves are nearly horizontal for D >10 nm. But the change in melting temperature is much rapid below 10 nmin case of these metallic nanostructuredmaterials. Again we can see that beyond 20 nm of the size of the material, the ratio of melting temperature at nanoscale to the bulk becomes almost constant. The universal relation for size dependent thermodynamic properties of metallic nanoparticles suggested by Xiong et al [6] also predict the same size dependent variation of melting point in case of metals. Also the change in melting temperature for nanosolids is larger than that of nanowires and nanofilms. This is due to the rapid increase in surface to volume ratio at smaller nanoscale.Our computed results are in good agreement with the experimental data obtained by Buffat [11] and Shim[12] who measured the melting temperatures using the scanning electron diffraction and evaporation rate measurement techniques, respectively.

An agreement between theoretical and experimental data encouraged us to extend this model to the Debye temperature. We have extended our study to the Debye temperature of these nanocrystalline structures. To study the size dependence of Debye temperature of selected samples we use equation (7) which is modified corresponding to the nanosolids, nanowires and nanofilms using equation (8-10). The computed theoretical values of Debye temperature of Cu, Pd, Pt and Al are plotted against the varying sizes of their nanostructures are shown in Fig. (5)-Fig. (8). From these figures, we can see that Debye temperature decreases with decrease in size of nanomaterials but this change in Debye temperature is less rapid than the melting temperature. This is because the Debye temperature varies as square root of melting temperature. For the size larger than 20 nm, the ratio of Debye temperature at nanoscale to the bulk material becomes almost constant, as shown the graphs. Similar to the variation of melting point with size the change in Debye temperature for nanosolids is larger than that of nanowires and nanofilms.

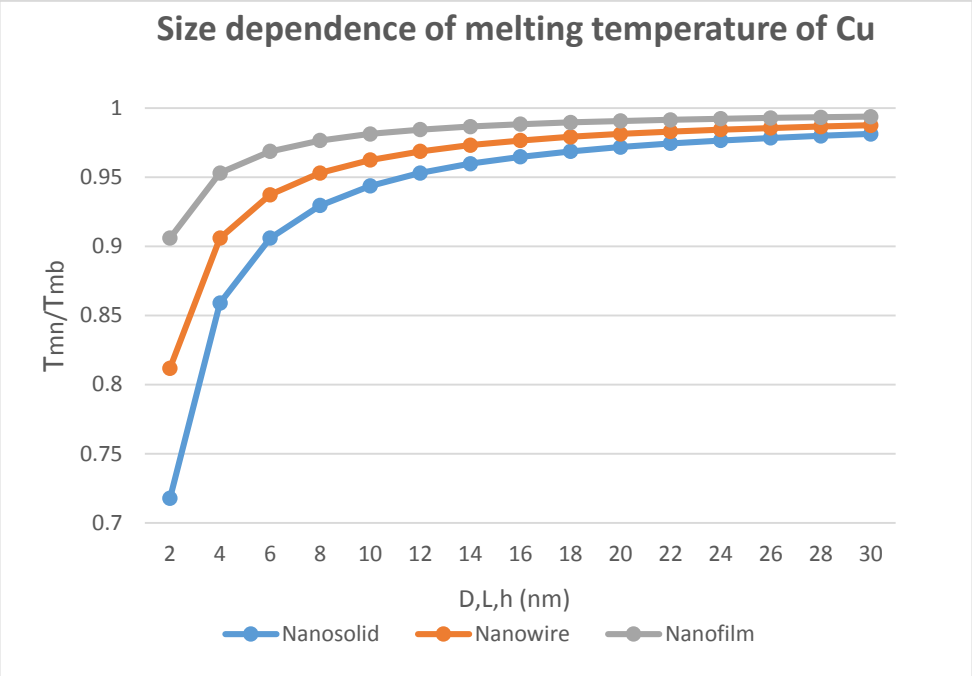

Fig. 1 Size dependence of melting point of nanocrystalline Copper (Cu)

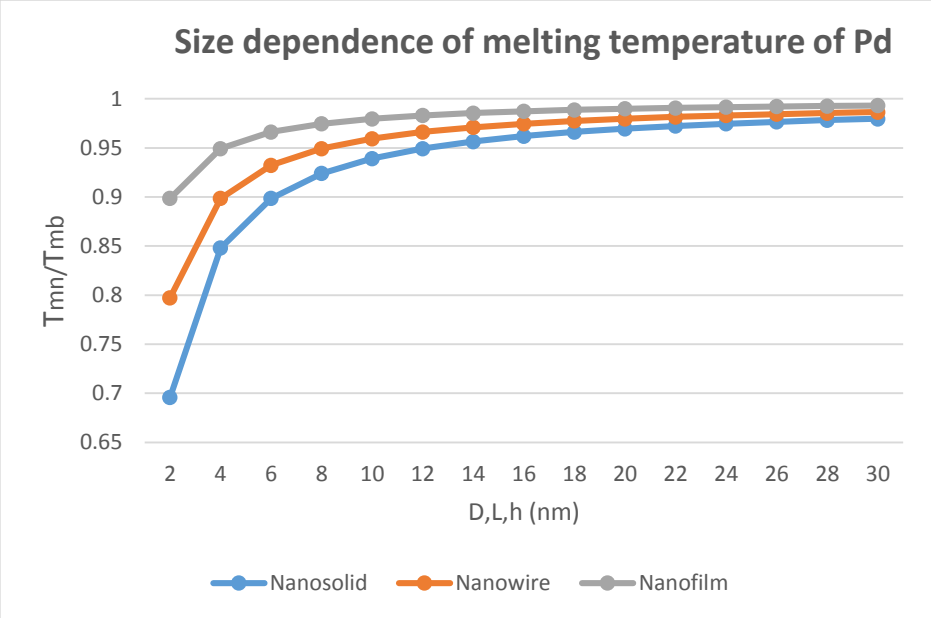

Fig. 2 Size dependence of melting point of nanocrystalline Palladium (Pd)

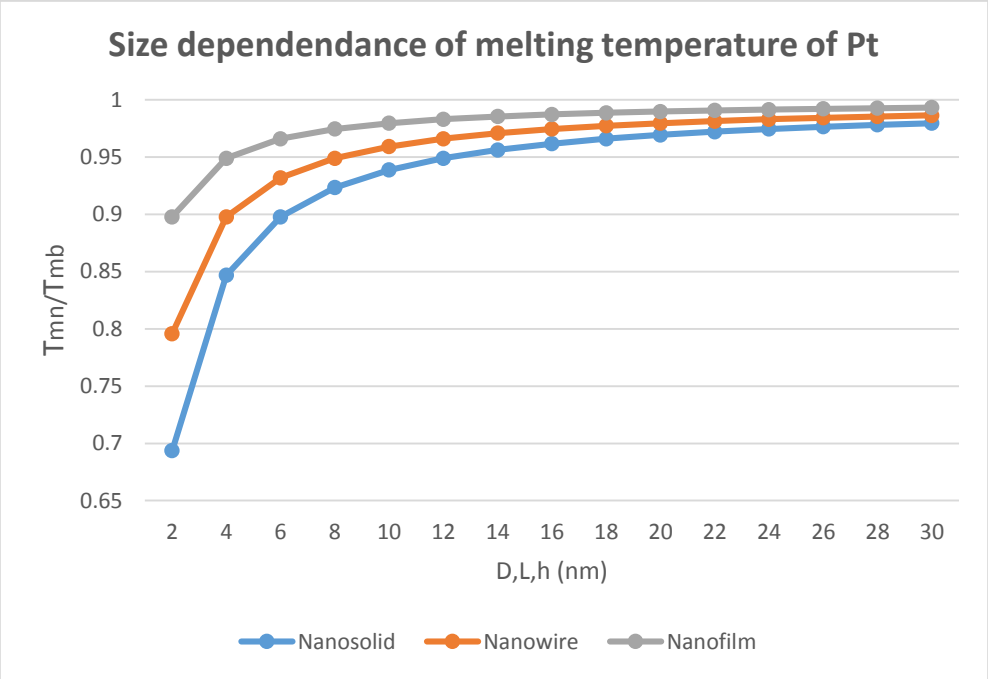

Fig.3 Size dependence of melting point of nanocrystalline Platinum (Pt)

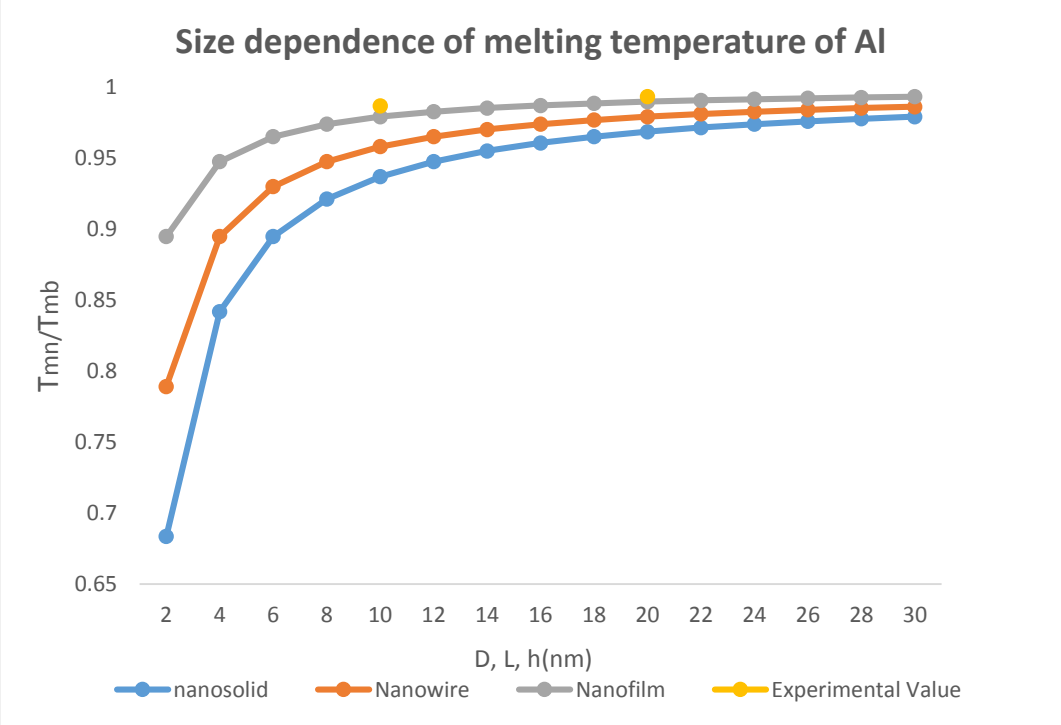

Fig. 4 Size dependence of melting point of nanocrystalline Aluminium (Al)

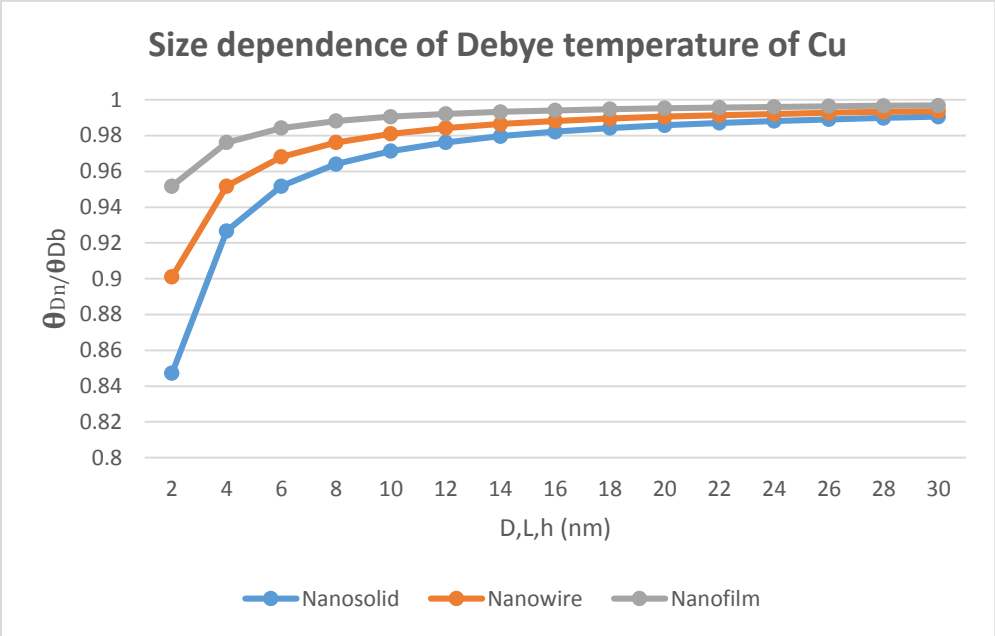

Fig. 5 Size dependence of Debye temperature of nanocrystalline Copper (Cu)

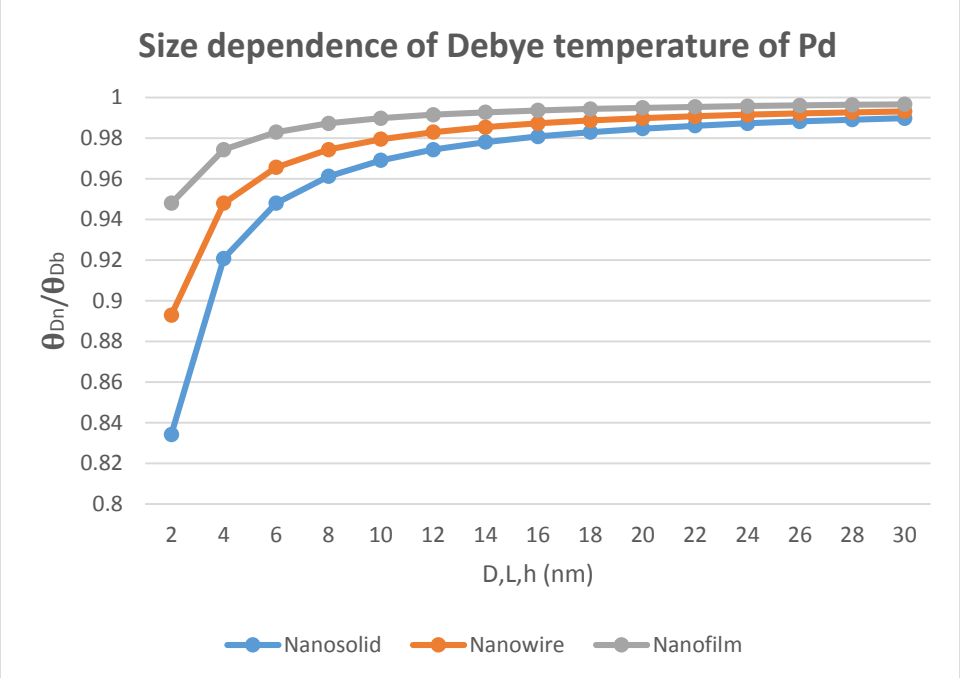

Fig. 6 Size dependence of Debye temperature of nanocrystalline Palladium (Pd)

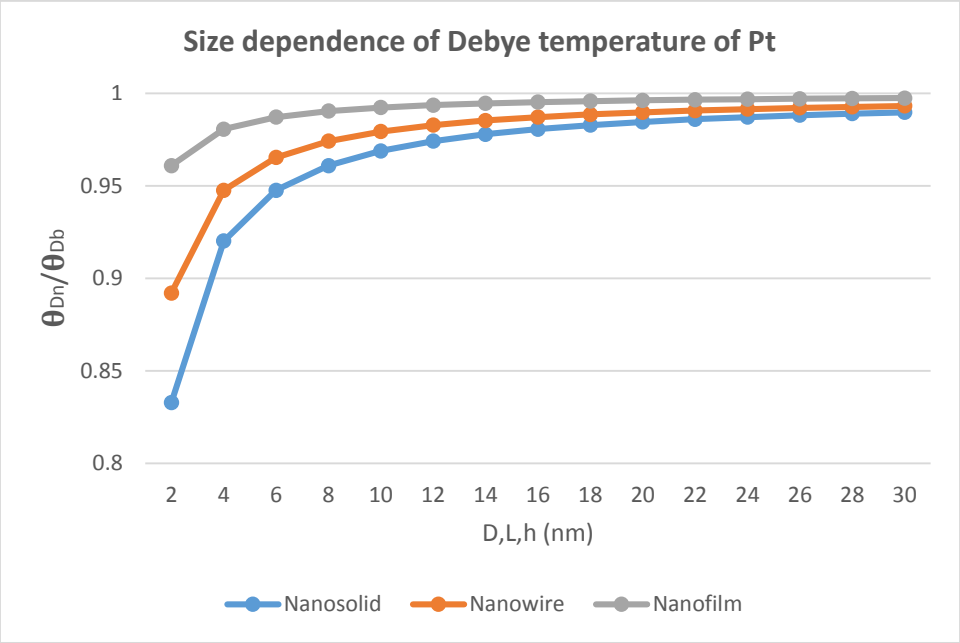

Fig. 7 Size dependence of Debye temperature of nanocrystalline Platinum (Pt)

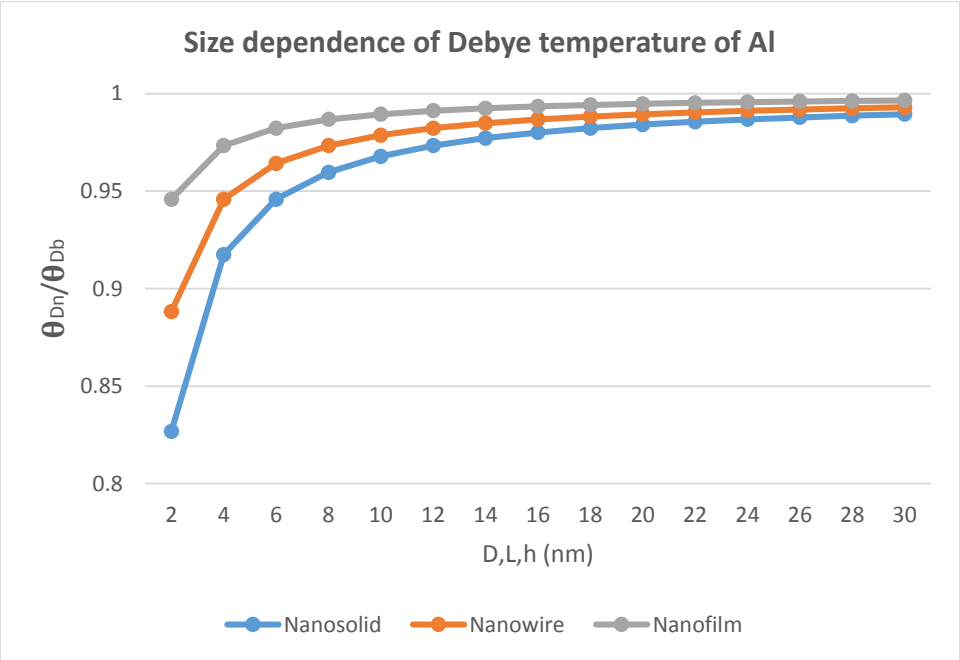

Fig. 8 Size dependence of Debye temperature of nanocrystalline Aluminum (Al)

4. CONCLUSION:

In case of metallic nanostructured materials melting temperature changes gently with the variation of size and the curves are nearly horizontal for D >10 nm, which becomes very much prominent below 10 nm. Beyond 20 nm of the size of the material, the ratio of melting temperature at nanoscale to the bulk becomes almost constant. The Debye temperature of metallic nanostructured materials also decreases with decrease in size of nanomaterials but this change in Debye temperature is less rapid than the melting temperature. This is because the Debye temperature varies as square root of melting temperature.

REFERENCES

[1] Poole P. Charles, Frank Jr., Owens J., 2008, Introduction to Nanotechnology, 2nd Edition, John Wiley and Sons, UCC Press, Delhi India.

[2] Pandey B. K., 2016, "Equation of State for the Compression of Nanocrystalline Anatase TiO_2" Der Pharma Chemica, 8(18), pp.163-167.

[3] Kittel C., 2008, Introduction to Solid State Physics, 7th Edition, John Wiley and Sons, Sonepat Haryana, India.

[4] Xiong Shiyun, Qi Weihong, Cheng Yajuan, Huang Baiyun, Wangand Mingpu, Li Yejun, 2011, "Modeling size effects on the surface free energy of metallic nanoparticles and nanocavities" Phys. Chem. Chem. Phys., 13, pp. 10652-10660.

[5] Bhatt J. C. & Kholiya K., 2014, "Effect of size on the elastic and thermodynamic properties of nanomaterials", Indian Journal of Pure & Applied Physics, 52, pp. 604-608.

[6] Qi. W. H., 2005, "Size effect on melting temperature of nanosolids" Physica B, 368, 46-50.

[7] Rose J. H., Ferranate J., Smith J. R.,1981, "Universal Binding Energy Curves for Metals and Bimetallic Interfaces", Phys. Rev. Lett., pp. 47, 675.

[8] Ferranate J., Rose J. H., Smith J. R., 1984, "Scaling relations in the equation of state, thermal expansion, and melting of metals" Appl. Phys. Lett., 44, pp.53-55.

[9] Lindemann F. A., 1910, "Physics of the Lindemann melting rule" Phys. Z, 11, 609.

[10] Sun J., Simon S.L., 2007, "Chemical Thermodynamics and Thermal Analysis", Thermo Chimica Acta., 463(1-2), pp. 32-40.

[11] Buffat Ph., and Borel J. P., 1976, "Size effect on the melting temperature of gold particles", Phys. Rev. A, 13, pp. 2287.

[12] Shim J. H., Lee B. J., and Cho Y. W., 2002, "Thermal stability of unsupported gold nanoparticle: a molecular dynamics study" Surf. Sci., 512(3), pp.262-263.