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# Effect of size and shape on the melting temperature , melting entropy and specific heat of  Silicon nanomaterial

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- ***Abstract:-***

A simple theory is proposed to study the size and shape dependent melting temperature, melting entropy, specific heat of nanomaterial’s. The particle size and shape are demonstrated to affect the melting temperature ,melting entropy ,specific heat the model is applied to Si nanomaterial's in spherical, nanowire and Nano films shapes. The specific heat is observed to increase with the decrease in particle size, whereas the melting entropy decrease as the particle size decreases. Our theoretical predictions agree well with available experimental and computer simulation results, thereby supporting the validity of formulation developed

- ***Introduction:-***

It has been reported that nanomaterial's exhibit interesting physical and chemical properties that are significantly different from the corresponding properties of bulk materials. Because of the enormous surface area to volume ratio of nanomaterial's , the energy associated with the atoms of these nanomaterial's will be different compared to that of conventional bulk materials, leading to the size-dependent thermodynamic properties of nanomaterial's. The cohesive energy, also known as the heat of sublimation, is an important physical quantity that accounts for the strength of metallic bonds, as it is the energy required to divide the metallic crystal into individual atoms. Experimental and theoretical studies of cohesive energy of Si nanoparticles have been conducted by many researchers. Modeling the size- and shape-dependent cohesive energy of nanoparticles and its applications in the heterogeneous systems has been calculated theoretically by Li, who reported that the cohesive energy of the free nanoparticles usually decreases as its size decreases. Considering the effects of particles size, lattice and surface packing factors and coordination numbers of the lattice, Shandiz et al.calculated the melting entropy and enthalpy of metallic nanoparticles. A theoretical study involving modeling of the melting enthalpy of nanomaterial's sought to define the conventional shape factor α. The melting temperature of Nano solids (such as nanoparticles, nanowires and Nano films) has been predicted based on size-dependent cohesive energy; it is shown that the melting temperature of nanomaterial's decreases with decreasing particle size. Researchers have calculated the root mean square amplitude model, the size-dependent Debye temperature model and size dependent thermal conductivity model by considering Lindeman's criterion and Mott's equation. and It is stated that the Debye temperature decreases for nanomaterial's as the size decreases. The effects of particle size and thermodynamic energy, based on surface thermodynamics and the atomic bond energy, were used to calculate the mechanical properties, such as surface tension and Young's modulus of Nano crystals. The cohesive energy is the basic thermodynamic property used to predict melting temperature, melting enthalpy, melting entropy specific heat of nanomaterial's. Scholars have proposed different models, namely the latent heat model, the liquid drop model and the surface area difference model, to predict cohesive energy of nanomaterial's . Recently, using

the concept of cohesive energy changes with the atomic coordination environment, presented a theory based on the bond energy model to highlights the thermodynamics for the nanoparticles, nanowires, and Nano films. The size and coherence dependent cohesive energy, melting temperature, melting enthalpy, vacancy formation energy and vacancy concentration of nanowires and Nano films have been reported .The variation direction of the thermodynamic properties is observed to be determined by the coherent interface and the quantity of variation depends upon the crystal size. Shandiz et al. developed a model for melting entropy and enthalpy of metallic nanoparticles, which is based on the effect of packing factors, coordination numbers of lattice and crystalline planes. Thus, it appears that there exist some attempts to study size-dependent thermo dynamical properties. Moreover, because the thermo dynamical properties also depend on the shape, it may be valuable to present a model that incorporates the effects of shape. In this contribution, we present a surface free energy model that does not use adjustable parameters and depends upon the size and shape with respect to the cohesive energy of nanomaterial's. Using the relationship between melting temperature and cohesive energy, the expressions for size- and shape-dependent specific heat, melting entropy and enthalpy are obtained. The theoretical predictions of these expressions are applied to Si nanomaterial's in spherical, nanowire and Nano films shapes

- ***Mythology:-***

The energy resulting from the contributions of the interior and surface atoms of the nanomaterial is known as the total cohesive energy and is expressed as:

$$E_{Total} = E_0(n - N) + \frac{1}{2}E_0N \ldots\ldots\ldots(1)$$

When the Nano solid's total atom count is n, and $N$ is the quantity of atoms on the surface. Hence, $(n - N)$ is a measure of how many internal atoms there are in a nanomaterial .The bulk material's cohesive energy, or $E_0$, is measured per atom .The cohesive energy per mole may be calculated using:

$$\frac{AE_{Total}}{n} = AE_0\left(1 - \frac{N}{n}\right) + \frac{1}{2n}AE_0N \ldots\ldots\ldots(2)$$

where $A$ is the Avogadro number. The relevant $AE_{Total}/n$ is the nanomaterial's cohesive energy per mole $E_n$, and The cohesive energy per mole of the related substance is $AE_0$.bulk substance $(E_b)$. When the appropriate parameters are substituted in Eq. (2), one may get:

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

According to a report, the cohesive energy and melting temperature are linearly related. As a result, we may express the relationship for the melting temperature of nanomaterial's as:

$$T_n = T_b\left(1 - \frac{N}{2n}\right)$$

where $T_b$ is the bulk material's melting point .For small particles, the Lindeman's melting criterion according to which a crystal melts when the root mean square displacement of atoms exceeds a predetermined percentage of the interatomic distance in the crystal is applicable. According to this theory, the bulk material's melting temperature and Debye temperature have the following relationship:

$$\theta_{Dn} \propto (\frac{T_b}{MV^{\frac{2}{3}}})^{1/2} \ldots\ldots\ldots(4)$$

where $V$ is the volume per atom and $M$ is the molecular mass. Similarly, the expression for nanomaterial's is

$$\theta_{Dn} \propto \left(\frac{T_n}{MV^{2/3}}\right)^{1/2} \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Eq. (3) and (5) give the following correlation:

$$\frac{\theta_{Dn}^2}{\theta_{Db}^2} = \frac{T_n}{T_b} \ldots\ldots\ldots\ldots(6)$$

A link between specific heat at constant pressure and the Debye temperature of bulk material is found using Debye's theory, that is,

$$C_{pb} \propto \frac{1}{\theta_{Db}^2} \ldots\ldots\ldots\ldots(7)$$

Similarly, for the nanomaterial's, the expression is

$$C_{pn} \propto \frac{1}{\theta_{Dn}^2} \ldots\ldots\ldots\ldots(8)$$

From Eqs. (6) (8), we obtain

$$\frac{C_{pn}}{C_{pb}} = \frac{T_n}{T_b} \ldots\ldots\ldots(9)$$

On substituting the value of Eq. (3) into Eq. (9), we obtain

$$C_{pn} = C_{pb}\left(1 - \frac{N}{2n}\right)^{-1} \ldots\ldots\ldots\ldots(10)$$

The link between the specific heat for bulk materials and nanoparticles in various forms and sizes is shown in the graph below. The melting entropy and enthalpy equations are then derived. The size dependence of their melting points can be used to compute the size dependence of the melting entropy of nanomaterial's. Metallic crystals' melting entropy is primarily of a vibrational character, and its electronic component is negligible. By taking into account the vibrational entropy as shown below, the link between melting entropy and melting temperature is derived:

$$S_{mn} = S_{mb} + \frac{3R}{2}\ln\frac{T_n}{T_b} \text{.....(11)}$$

where $R$ is the gas constant; $S_{mn}$ and $S_{mb}$ are the melting entropy of nanomaterial's and bulk materials, respectively. From Eqs. (3) and (11), we obtain

$$S_{mn} = S_{mb} + \frac{3R}{2}\ln\left(1 - \frac{N}{2n}\right) \ldots\ldots\ldots (12)$$

The melting enthalpy and melting entropy for bulk materials follow the relationship given below:

$$H_{mb} = T_b S_{mb} \ldots\ldots\ldots\ldots (13)$$

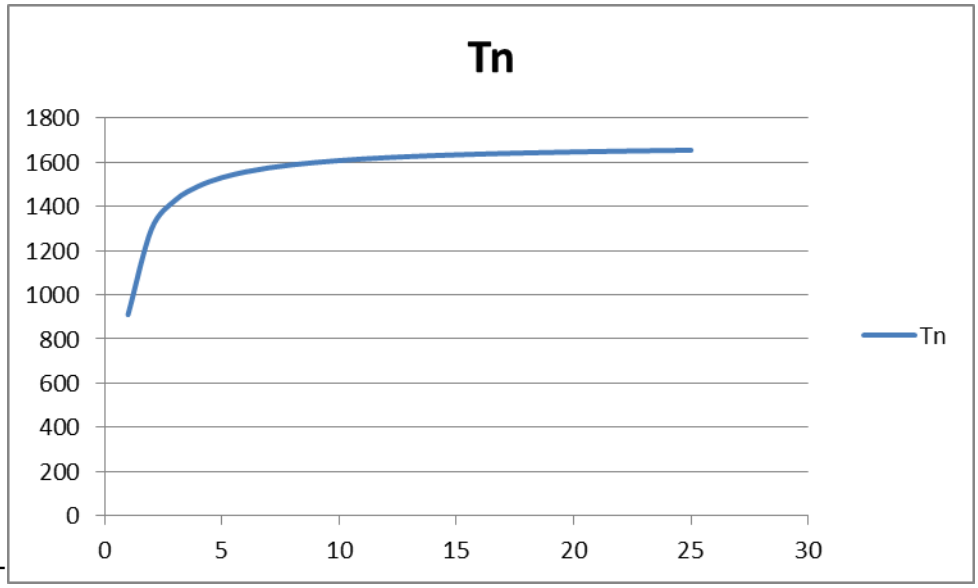
Assuming this relationship is still valid in nanomaterial's, we can write

$$H_{mn} = T_n S_{mn} \ldots\ldots\ldots\ldots (14)$$

Substituting the values of Eqs. (3) and (12) into Eq.(14) and rearranging, we obtain

$$H_{mn} = \left(H_{mb} + \frac{3RT_b}{2}\ln\left(1 - \frac{N}{2n}\right)\right)\left(1 - \frac{N}{2n}\right) \ldots\ldots (15)$$

The approach has already been documented in the literature for $N/2n$ values. The size and shape of the nanoparticles affect the value of $N/2n$. For spherical Nano solids, the value of $N/2n$ is equal to $2d/D$, where $d$ is the diameter of an atom and $D$ is the diameter of the spherical Nano solids. The values of $N/2n$ for nanowire and Nano film, where $l$ is the diameter of the nanowire and $h$ is the width of the Nano film, respectively, are $4d/3l$ and $2d/3h$.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