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RESEARCH PAPER

Lattice structure effect on some thermodynamical properties of Si Nanoparticles

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ABSTRACT:

An approach is made to calculate and analyze some thermodynamical properties including the combination of Lindemann's role for melting, dimensionless mass, and structure factor in the role of lattice structure as the mean bond length to examine their dependency in group IV elements and SiC tetrahedral semiconductors. The results were a direct relation for Lindemann's ratio (f) ad dimensionless mass μ with these materials mean bond length (d_{mean}) in the form of $f = 0.214 d_{mean}^{-1}$ and $\mu = 435 d_{mean}{}^{2}$ respectively. From the modification of these relations, the nanosize dependence for both Lindemann's ratio and dimensionless mass with that of the materials structure factor was calculated. The results are a decrease in Lindemann's ratio and an increase in the dimensionless mass with the size decrease of Si nanoparticles.

KEY WORDS: Nanoparticles, Lindeman's ratio for melting, Dimensionless mass, Tetrahedral semiconductors, Si.
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1.INTRODUCTION :

Recently, a lot of focus has been placed on theoretical investigations, synthesis, and applications of nanoscale semiconductors, which are crucial components of several emerging technologies. Due to their enormous surface area or the quantum size effect, semiconductor materials exhibit unique physical characteristics when their size is lowered to the nanoscale [1-5]. In this instance, researchers are attempting to comprehend how the material characteristics alter as a result of scaling down the nanosize to several atomic diameters [2]. Group IV elements' characteristics including mechanical, electrical, optical, and thermal properties have all undergone extensive study, but at the nanoscale, further research is needed, and obtaining accurate value for many of their physical properties remains difficult and important. The majority of these bulk material characteristics stay constant at a given temperature. However, for a nanoscale range crystal, these characteristics will be strongly impacted by the material's size [1].

Based on the mean bond length dependency on the size of the nanoscale materials, an attempt is made to modify the empirical relation obtained from the lattice size dependence of Lindemann's ratio and dimensionless mass for elements forming group IV and SiC to that of the nanoscale size states of the solid.

According to Lindemann's theory, the substance melts when its atomic motion's vibrational amplitude reaches a particular fraction of the lattice's interatomic distance. (A. Lawson, 2001; A. Lawson, Martinez, Roberts, Bennett, & Richardson Jr, 2000). This thermal vibration amplitude at the melting point is connected to Tm through the Lindemann rule; the amplitude could be calculated using the elastic characteristics measured at the melting point (A. Lawson, 2001; A. Lawson et al., 2000; A. C. Lawson, 2009).

Although according to Lindemann's role, this ratio is about 10% for all solids but was later reported to be dependent on the materials type and its melting temperature [9, 10]. In this work attempts are made to investigate and calculate the lattice structure dependence of Lindemann's ratio,

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dimensionless mass, and materials structure factor in a systematic form for group IV elements and SiC. The dependence will be modified for applications on the nanoscale size dependence of these parameters in Si nanoparticles as an example.

2. Methods of Calculation;

Based on the principals constructed by [11, 12, 13] Cho 1978, derived a relation to calculate lattices root mean square displacement in solids at the melting temperature as in the following [14]:

$$< U_i^2 >= {9h^2T_m}\Big/{4\pi^2 k_B m\theta_D^2} \qquad (1)$$

For h, T_m, k_B, m, and θ_D are Plank's constant, melting temperature, Boltzmann's constant, atomic mass and the Debye temperature respectively.

The ratio of root mean displacement at the melting temperature to that of inter-atomic distance in this work refereed by mean bond length (d_{mean}) in the form of $< U >\big/ d_{mean} = f$, it is called Lindemann's ratio for melting, that is accordingly from Eq. (1) will get the form;

$$f = \left({9T_m h^2}\Big/{4dmean^2 \pi^2 kM\theta^2} \right)^{0.5} \qquad (2)$$

Table 1 gives all the parameters used to calculate f and its value for all elements forming group IV and SiC.

Table. 1 Atomic mass (M x 1.66 x 10^{-27}Kg), Debye temperature (θ_D in K), Melting temperature (T_m in K), mean bond length (d_{mean} in 10^{-10}m), Lindemann's ratio of melting (f), dimensionless mass (μ) Structure factor (A_{Stru}) and Bond energy (E_b in eV) for group IV elements and SiC.

Elements	M	Θ_D	T_m	d_{mean}	f	μ	A_{Stru}	E_b[20]
C	12	1860[15]	3800[17]	1.545	0.134	945	0.419	-30.87
SiC	20.048	1200[16]	3100[19]	1.88	0.115	1561	0.4016	-21.21
Si	28.085	711[17]	1683	2.35	0.096	2064	0.355	-13.3
					0.124[1]	1280[7]		
Ge	73	374[17]	1209	2.45	0.092	3016 2999	0.3588	-12.27
Sn	118.7[22]	199[18]	505	2.81	0.077	3406	0.3066	-9.32

The Lindemann's ratio for these elements and SiC is drawn versus their mean bond length as shown in the following figure.

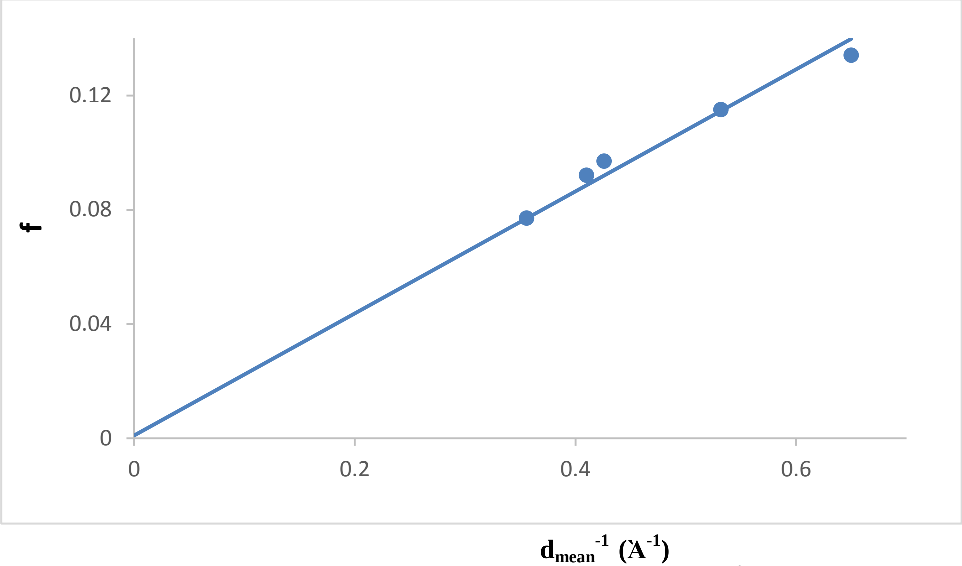

Fig. 1 Lindemann's ratio dependence on elements reciprocal mean bond length forming group IV semiconductors and SiC

The fitting curve for the dependence in this figure gives the following relation:

$$f = 0.214(d_{mean})^{-1} \qquad (3)$$

Introducing the dimensionless variable $x_0 = (3\hbar^2)/2mV^{2/3}k_B\,\theta_D$[6], this is the ratio of zero-point vibrational energy to Deit's energy, its reciprocal representing the dimensionless mass denoted by μ as in the following [7]:

$$\mu = m\frac{2{d_{mean}}^2 k_B\,\theta_D}{3\hbar^2} \qquad (4)$$

Values of μ for all elements and compounds interested in this work are presented in tTable1. The dependence of μ on mean bond length is shown in Figure 2

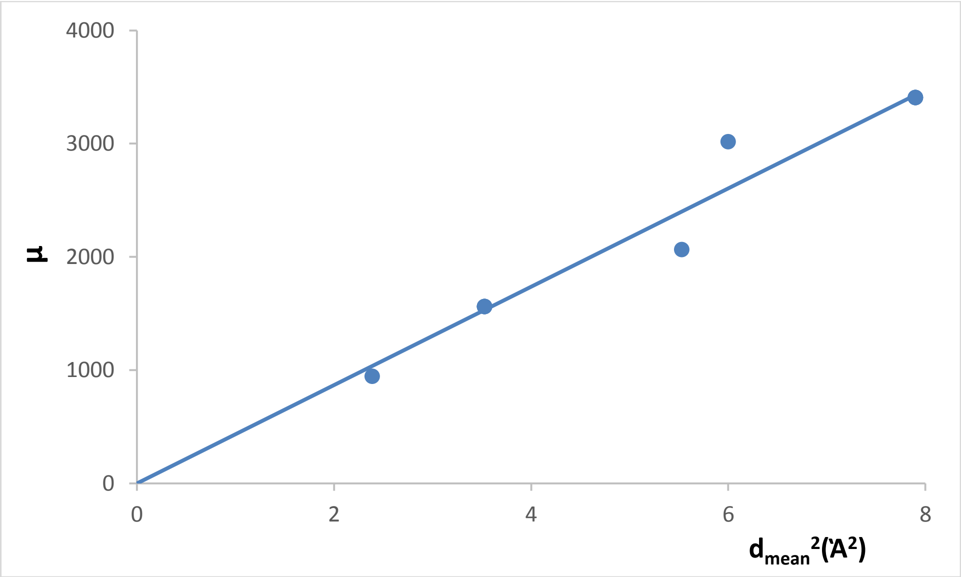

Fig. 2 Dimensionless mass dependence on square mean bond length for group IV elements and SiC

The fitting curve to the dependence in Figure 2 gives the following form:

$$\mu = 435{d_{mean}}^2 \qquad (5)$$

To investigate the effects of structure on thermodynamical properties in solids, Lawson 2001 [7], has found a specific dependence in the form $A(structure) = f\mu^{0\cdot17}$ in which from, the crystal structure factor which is denoted by (A), calculated for all elements interested in this work as the results are given in table 1.

It is well known that the material's properties are affected strongly by the change in their size particularly in the nanoscale range [1-5]. Since the material's properties are controlled by their structure which is in this work denoted by $d_{mean}(\infty)$, hence (∞) refers to materials bulk state, which is used to calculate the nanosize dependence parameters. The equations to calculate the nanosize dependence of f, μ and $A(structure)$ are modified as in the following:

$$f(r) = 0.214 d_{mean}(r)^{-1} \qquad (6)$$

$$\mu(r) = 435 d_{mean}(r)^{2} \qquad (7)$$

And

$$A_{Stru}(r) = f(r)\mu(r)^{0\cdot 17} \qquad (8)$$

Hence (r) refers to the nanoscale form of the material.

In equations (6) and (7), the nanosize dependence $d_{mean}(r)$ can be calculated according to [3, 4], $d_{mean}(r) = h - \Delta d_{mean}(r)$, h is the first solid surface layer height, it is calculated by using the relation $h = 1.429 d_{mean}$ and $\Delta d_{mean}(r)$ determined from (Omar, 2016):

$$\Delta d_{mean}(r) = d_{mean}(r_c)\left[e\left[\frac{-2(\square m-R)}{3R\left[\left(\frac{r}{rc}\right)-1\right]}\right]\right]^{\frac{1}{2}} \qquad (9)$$

where $\Delta d_{mean}(r_c) = h - d_{mean}(\infty)$, □m is the bulk overall melting entropy in (J ▪ K^{-1} ▪ mol^{-1}), R is the ideal gas constant equal to (8.314 J ▪ K−1 ▪ mol−1), r is the radius of the nanoparticle and r_c is the critical radius in which the material melt at zero Kelvin.

Accordingly, the nanosize dependence of $f(r)$, $\mu(r)$ and $A_{Stru}(r)$ for Si as an example are drawn as in the following figures;

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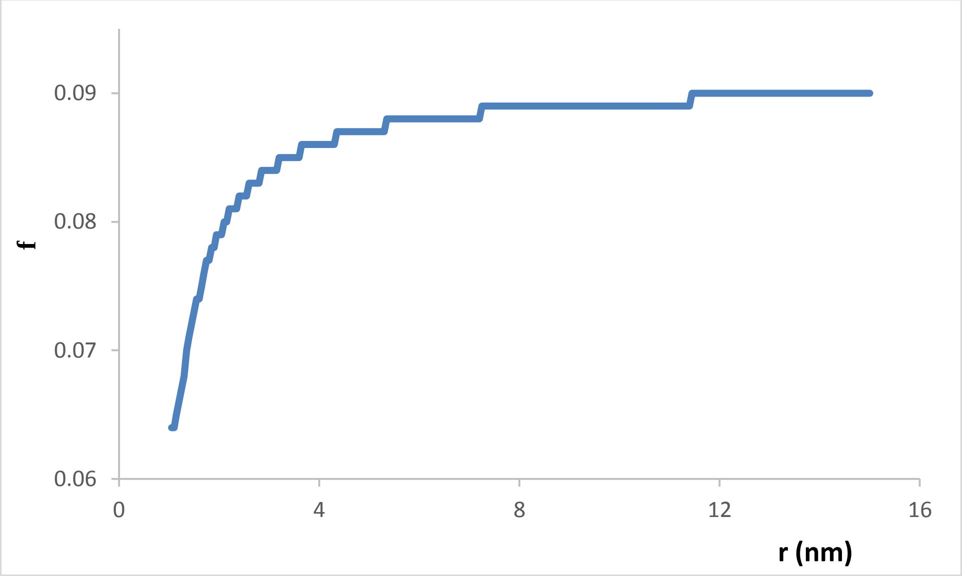

Fig. 3 The nanosize dependence of Lindemann’s ratio for Si particles

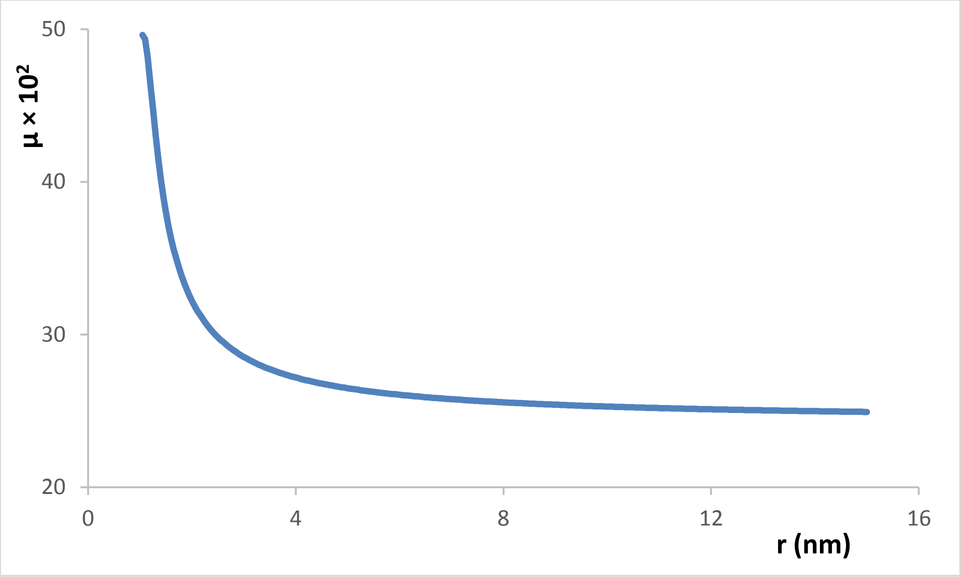

Fig. 4 The nanosize dependence of dimensionless mass for Si particles

Recalling Lawson's law in relating both dimensionless mass and Lindemann's ratio, the nanoscale structures parameter dependence on size for Si as an example is calculated from the modification as in the following figure;

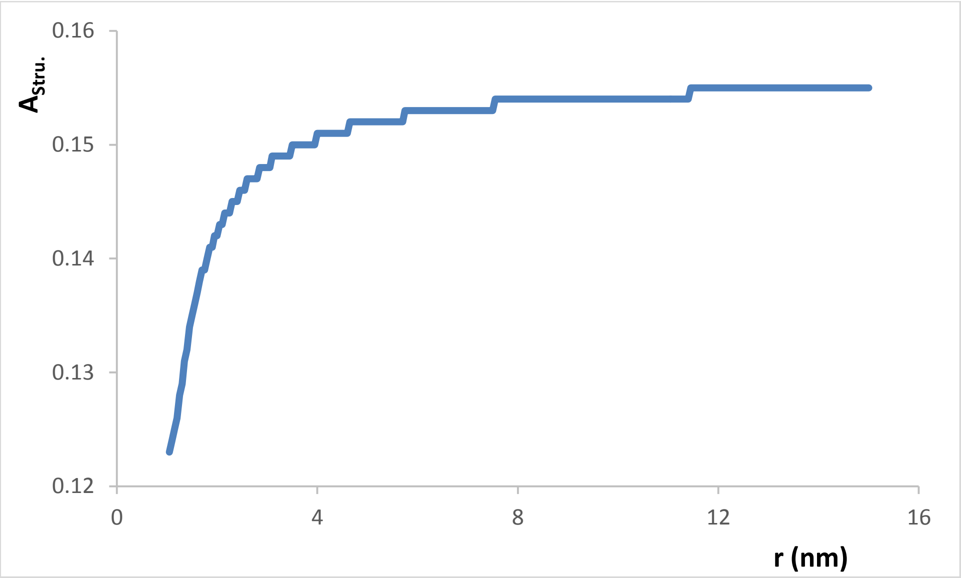

Fig. 5 The nanosize dependence of structure factor for Si particles

3-Analysis of results

All the physics parameters for solid materials have a direct or indirect dependence on the material's lattice structure [21-23]. In this work, the decrease in the linear dependence of Lindemann's ratio for group IV and SiC with their reciprocal mean bond length can be explained according to the bond energy interaction of elements. Larger atoms "Sn" with lower bond energy have a smaller interaction between atoms, followed by a smaller mean square displacement and a smaller Lindemann's ratio. In this case, carbon has the largest energy bond interaction followed by the highest Lindemann's ratio value. To explain the dependence in Figure 1, the increase in mean bond length between atoms reduces lattice vibrational amplitudes. However, Omar etal 2023, reported the decrease of lattice anharmonicity L_{an} for bulk Si with the increase of the lattice volume in the form of $L_{an} =$

$1.56\left(\frac{V}{V_0}\right)^{-1.67}$, V is the lattice volume under pressure and V_0 for a zero pressure [1].
The decrease of Lindemann’s ratio in the solid’s nanoscale size dependence given in Figure 3, which is calculated according to Eq. (6), refers to the decrease of lattice energy bond interaction as explained above. In this case, the increase of mean bond length with the nanoparticles size reduction explains the reduction in the materials lattice bond energy shown in Table 1.

The increase of dimensional mass according to Figure 2 with the material's mean bond length forming group IV elements and SiC may refer to restoring the reduction of energies needed for solid bonds. In this case, elements with larger bond lengths have higher dimensionless mass values such as Sn, in the other way, C with a lesser value has the highest bond energy among these group elements. Equation (7), the modification to Eq. (5) its dependence as shown in Fig. 4, refer to the decrease in the energies need for bonding by reducing the nanoparticle's size. The larger the lattice mean bond length represents their lesser lattice interaction, followed by the less energy needed for bonding. The latter is followed by the decrease of the materials melting temperature which is true for different elements in their bulk state for group IV as an example as shown in table 1.

According to the dependence above, the reduction in the nanosize scale that follows by decreasing the materials melting temperature [1-5], can also consequently be referred to by the reduction in the materials lattices bond energy [22].

To explain how the structure of the material specifies the material properties, Lawson 2001 [7], reported the following dependence $A_{Stru} = f\mu^{0\cdot 17}$. Fig. 5, which is obtained from the nanosize dependence modification, the decrease of $A_{Stru}(r)$ with the size reduction refers to the loss in materials structure combination [2] since both f and μ are a structure dependent parameter.

Conclusion

The dependence of Lindemann’s ratio for bulk elements forming group IV and SiC gives a structure dependence related parameter denoted by the material's mean bond length. Modifications for this dependence were successful to calculate the nanosize dependence Lindemann’s ratio. Its decrease with the reduction of particle size explains well the structure control of thermodynamical properties in both bulk state and the nanoscale solids. The dimensionless mass values increase with the decrease of nanoscale size particles, the dependence explains well the materials with larger bond length, the case for smaller size nanoparticles will have a lesser value need for bonding and consequently increasing lattice degree of freedom.

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