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EFFECT OF GRAIN SIZE ON VOLUME THERMAL EXPANSION OF NANOMATERIALS

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ABSTRACT

Size effects on Volume thermal expansion of nanomaterials. The experimental measurements show that volume thermal expansion of nanosolids is larger than those of their bulk counterparts. On considering the surface effect, a simple model is derived to study the size dependence of volume thermal expansion of nanomaterials for spherical nanoparticles, nanowire and nanofilms. The size dependence of Zn nanowire is found to present the good agreement with the existing experimental results. We have also computed the size dependence volume thermal expansion of Si and Ni for spherical nanosolids, nanowires and nanofilms. It is shown that volume thermal expansion of nanomaterials decreases with increase in the grain size.

Keywords: Size Effect, Cohesive Energy, Thermal Expansion, Nanosolids

I INTRODUCTION

Size affects the thermoelastic properties of the nanosolids. A substantial research has been done on understanding their physical and chemical properties of the nanosolids[1]. Nanomaterials with particle size of 1-100 nm are of current interest because they show noble physical and chemical properties that may differ from those of the corresponding bulkcounterparts[2]. Nanosolids can be the spherical nanosolids, nanowires or nanofilms. Many physical properties such as hardness, melting temperature, sintering ability and electronic structure may be dependent upon the particle size[3].Gold and silver at nanosize have proven many chemical and physical properties. It is observed that elastic modulus and melting point change linearly with the inverse of size of nanomaterials[4]. Theoretical reconciliation of the observed size dependence of the lattice strain, elastic modulus and melting point for Ag and Au nanostructures can be understood by the theory of under-coordination[5]. Chang *et al.*[6] observed that the volume thermal expansion of Cu nanomaterial is three times the linear thermal expansion irrespective to the crystal orientations. Molecular dynamics simulation to study the thermomechanical properties of copper nanofilm is studied at different temperatures[7]. Thermal expansion coefficient of Zn nanowire was measured using the *in situ* high resolution X-ray diffraction technique[8]. Qi[9] calculated the size dependent melting temperature of Pb, Sn, and In nanoparticles using the theory that the cohesive energy of the nanosolids is the sum of interior atoms and the surface atoms, which is read as

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

Where n is the total number of nanoatoms, N is the total number of surface atoms and E_0 is the cohesive energy per atom of the bulk material. Eq. (1) is redefined as

$$E_p = E_b\left(1 - \frac{N}{2n}\right), \qquad (2)$$

Where $E_p = \frac{AE_{Total}}{n}$, $E_b = AE_0$ and A is the Avogadro constant. Cohesive energy and melting temperature both describe the bond strength of the materials. Rose *et al.*[10] stated the linear relation of cohesive and melting temperature of the materials. Since N/n of nanosolid is a function of cohesive energy, so the relation developed for melting temperature is as follows[9]

$$T_p = T_b\left(1 - \frac{N}{2n}\right), \qquad (3)$$

T_p And T_b are defined as the melting temperature of nanosolid and corresponding bulk modulus respectively. Using Eq. (3) Qi[9] calculated the melting temperature of Sn, Pb and In nanosolids and it is shown that the melting temperature of the noanosolids decreases with decrease in solid size.

Thermoelastic properties of the nanomaterials depend upon the size of the particle. Experimentally, it is shown that the thermal expansion coefficient of nanomaterials is greater than that of their bulk equivalents. In the present work, we discussed a relation of volume thermal expansion V/V_0 for Zn, Si and Ni nanosolids viz. spherical nanosolids, nanowires and nanofilms with free surface. The efficiency of the model is confirmed by the available experimental data.

II METHOD OF ANALYSIS

Using molecular dynamics simulation, Prakash*et al.*[11] determined α of a single wall carbon nano tubes (CNT) and used the temperature dependence of α as:

$$\alpha = a + bT + cT^2, \qquad (4)$$

One canwrite Eq. (4), in order to satisfy the initial boundary condition as follow:

$$\alpha = a + b(T - T_0) + c(T - T_0)^2,$$

$$\text{Or, } \alpha = \alpha_0 + \alpha_0^{'}(T - T_0) + \alpha_0^{''}(T - T_0)^2, \qquad (5)$$

The first and second order derivatives of α with T are defined by α' and α''. It is possible to define $\alpha_0^{'}$ and $\alpha_0^{''}$ in terms of α_0, which reads as follows[12]:

$$\alpha_0^{'} = \alpha_0^2\delta_T,$$

And, $\alpha_0^{''} = \alpha_0^3\delta_T^2$,

Where, δ_T is the Anderson parameter and suffix 0 refers to the reference condition. So, Eq. (5) is written as

$$\alpha = \alpha_0 + \alpha_0^2 \delta_T (T - T_0) + \alpha_0^3 \delta_T^2 (T - T_0)^2 , \quad (6)$$

In fact Eq. (6) is an incomplete equation in which higher order terms are excluded. On including all the higher order terms in Eq. (6), it becomes:

$$\alpha = \alpha_0 + \alpha_0^2 \delta_T (T - T_0) + \alpha_0^3 \delta_T^2 (T - T_0)^2 + \alpha_0^4 \delta_T^3 (T - T)^3 + ... + \ldots$$

Or, $$\frac{\alpha}{\alpha_0} = \{1 - \alpha_0 \delta_T (T - T_0)\}^{-1} , \quad (7)$$

By definition of thermal expansion coefficients which is read as

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right) \quad (8)$$

From equation (7) and (8), one can get

$$V = V_0 \left(\frac{1}{1 - \delta_T \alpha_0 (T - T_0)}\right)^{\frac{1}{\delta_T}} , \quad (9)$$

Where, V_0 and α_0 are the reference value of the volume expansion and coefficient of thermal expansion respectively. For simplicity one can write α_0 as α_p, which is a size and shape dependent parameter. Kumar *et al.*[13] derived the relation for α_p, which is read as

$$\alpha_p = \alpha_b \left(1 - \frac{N}{2n}\right)^{-1} , \quad (10)$$

N is the total number of surface atoms and n is the total number of nanosolids. α_b is coefficient of volume thermal expansion of bulk material. The surface atoms refer to the first layer of the nanosolid. The method to find $N/2n$ for different shape of nanomaterials has been discussed by He*et al.*[12]. The expression of $N/2n$ has been tabulated in Table 1. Where, D is the diameter of spherical nonosolid, d is the diameter of atom, l is the length of nanowire and h is the height of nanofilm.

Table 1. $N/2n$ **For Different Nanosolids**[12]

Nanomaterials	N/2n
Spherical Nanosolids	2d/D
Nanowires	4d/3l
Nanofilms	2d/3h

Table 2. Input Parameters[8,14]

Nanomaterials	α_b ($10^{-5}K^{-1}$)	d(in nm)
Zn	0.54	0.495
Si	0.3	0.337
Ni	3.3	0.248

From Eqs. (9-10), the general expression for V/V_0 becomes as:

$$\frac{V}{V_0} = \{1 - \alpha_b \delta_T (1 - \frac{N}{2n})^{-1} (T - T_0) \}^{-1/\delta_T}, \quad (11)$$

Putting the values of N/2n From Table 1 in Eq. (11), the expressions for V/V_0 for different shape and size of nanosolids become as:

For spherical Nanosolid

$$\frac{V}{V_0} = \{1 - \alpha_b \delta_T (1 - \frac{2d}{D})^{-1} (T - T_0) \}^{-1/\delta_T}, \quad (12)$$

For Nanowire

$$\frac{V}{V_0} = \{1 - \alpha_b \delta_T (1 - \frac{4d}{3L})^{-1} (T - T_0) \}^{-1/\delta_T}, \quad (13)$$

And for Nanofilm

$$\frac{V}{V_0} = \{1 - \alpha_b \delta_T (1 - \frac{2d}{3h})^{-1} (T - T_0) \}^{-1/\delta_T}, \quad (14)$$

In the present paper, we use Eqs. (12-14) to study the temperature and size dependence volume thermal expansion for different nanomaterials.Throughout the calculation the value of δ_T is taken four as discussed by Kumar and Kumar[15]. Using Eqs. (12-14) and input parameter as given in Table 2, we calculated the V/V_0 of Zn, Si, Ni nanosolids in different forms for spherical nanoparticles, nanowire and nanofilms.

III RESULTS AND DISCUSSION

The grain size dependence volume thermal expansion (V/V_0) of Zn, Si and Ni nanomaterials has been calculated from Eqs. (12-14) from the room temperature to the higher temperature. A positive volume thermal expansion is noted in all nanomaterials in different shapes (spherical, nanowire, and nanofilm), which may be understood by the effects of the anharmonic lattice potential on the equilibrium lattice separations and characterized by the Gruneisen parameter[16]. The results are reported in the Figs. 1-7 along with the available experimental data. For comparison purpose we also included the temperature dependence bulk materials also. Experimentally thermal expansion coefficient of Zn nanowires were measured by high resolution XRD with temperature[8]. V/V_0 is

calculated using Eq. (13) for the Zn nanowire (40 nm) and it is reported in the Fig 1 along with the available experimental data[8]. It is seen from the figure that up to the temperature about 600 K; our results are very close to the experimental data. Beyond 600 K, there is a slightly change with the experimental records.Figs. 2-4 predict the size dependence V/V_0 of Si nanomaterials from temperature 300 K to 1050 K for different shapes, viz. spherical nanosolid, nanowire and nanofilm along with the temperature dependence bulk materials.In fig. 2 temperature dependence of Si nanomaterial in spherical shape at 10nm, 25 nm and 50nm is presented. It is clear from the plot that the as grain size decreases, volume thermal expansion increases with increase in temperature and the value is higher as compared to the bulk materials. From figs. 2-4, it is clear that as the shape is changing from spherical nanosolid to nanowire to nanofilm, the impact of size is decreasing. However, in all cases it is slightly greater than bulk materials. The theoretical predictions for Ni for different shape (spherical nanosolid, nanowire, nanofilm) are presented in the Figs. 5-7.It is established that as the size is decreasing volume thermal expansion increasing. The present theory is mainly to deal with the volume thermal expansion of nanosolids with free surface.

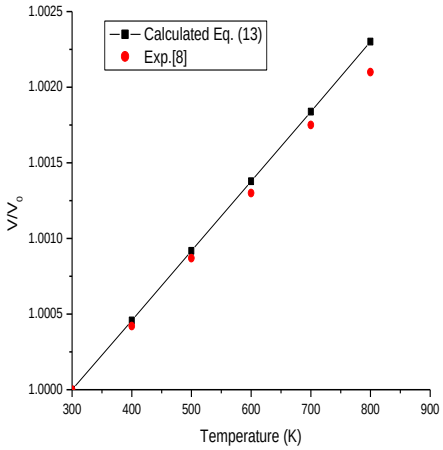

Fig.1, Temperature dependence of Zn nanowire(40nm)

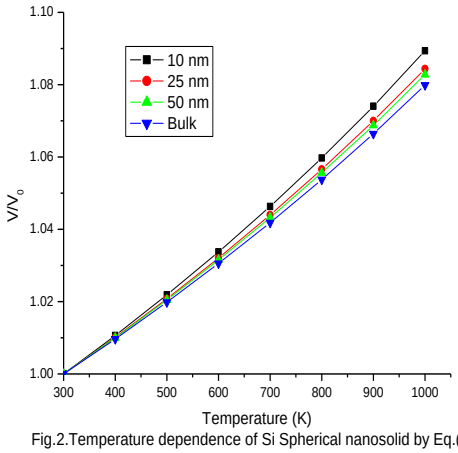

Fig.2.Temperature dependence of Si Spherical nanosolid by Eq.(12)

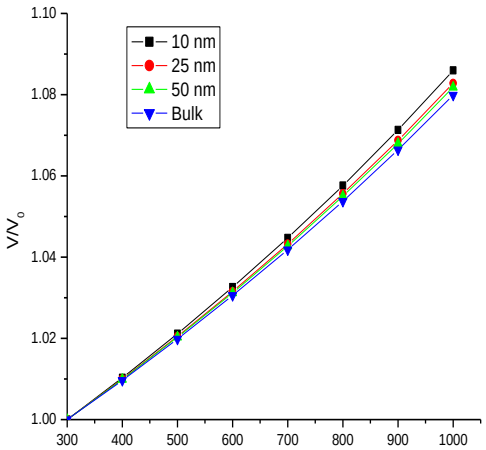

Fig.3. Temperature dependence of Si nanowire by Eq.(13)

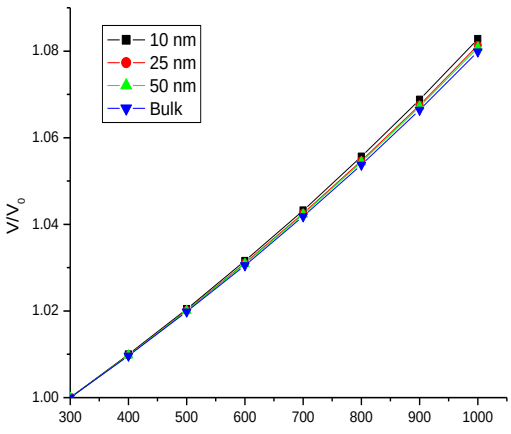

Fig.4.Temperature dependence of Si nanofilm by Eq. (14)

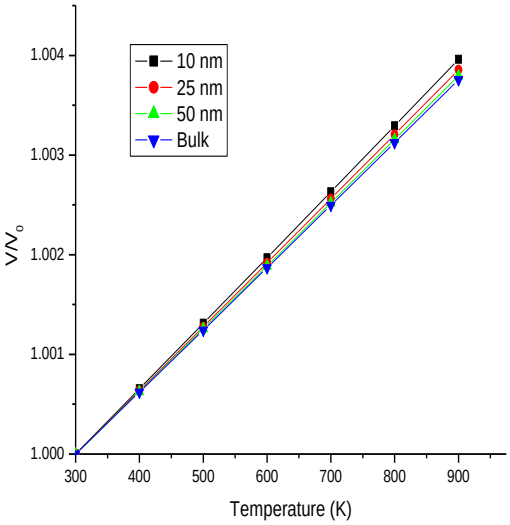

Fig.5.Temperature dependence of Ni Spherical nanosolid by Eq.(12)

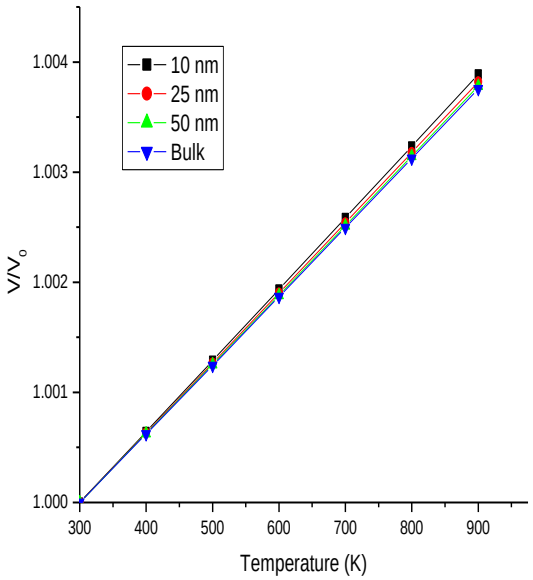

Fig.6.Temperature dependence of Ni nanowire by Eq. (13)

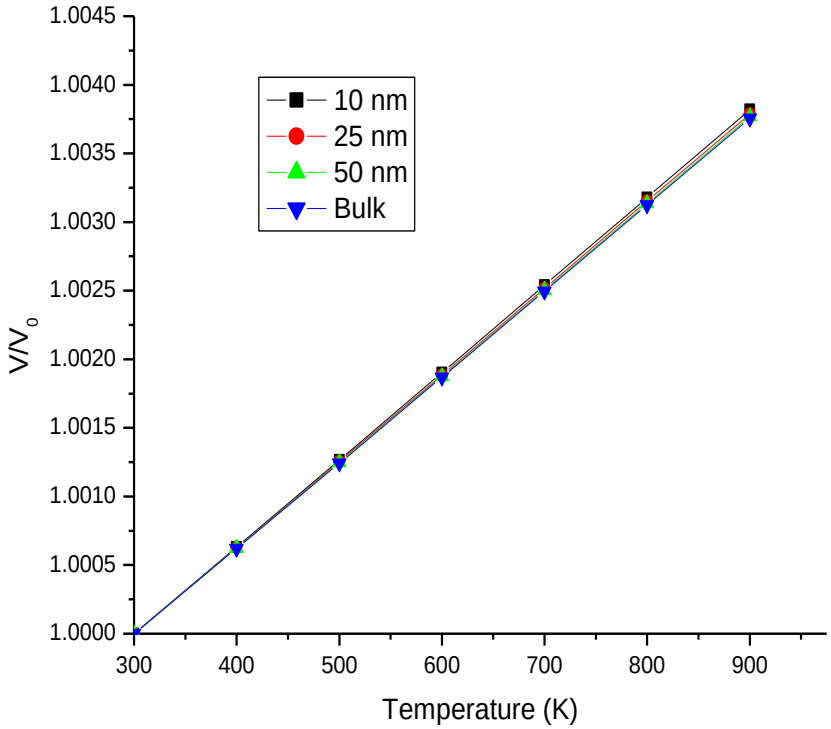

Fig.7.Temperature dependence of Ni nanofilm by Eq.(14)

IV CONCLUSIONS

A simple theoretical method is discussed to calculate the volume thermal expansion for spherical nanosolid, nanowire and nanofilm. The method has been derived on the bases of the concept of thermal expansion as discussed by Prakash[11] and the theory of cohesive energy as discussed by Qi[9]of the nanosolids. It is reported from the theory that thermal expansion increases with decreasing grain size. The method presented in this paper may have potential application in the research of temperature and size dependent properties of nanomaterials.

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