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Shape, size and temperature dependency of thermal expansion, lattice parameter and bulk modulus in nanomaterials

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Abstract. A theoretical model is described here for studying the effect of temperature on nanomaterials. The thermodynamic equation of state (EoS) proposed by Goyal and Gupta in *High Temp.-High Press.* **45**, 163 (2016); *Oriental J. Chem.* **32**(**4**), 2193 (2016), is extended in the present study using Qi and Wang model [*Mater. Chem. Phys.* **88**, 280 (2004)]. The thermal expansion coefficient is expressed in terms of shape and size and used to obtain the isobaric EoS of nanomaterials for the change in volume V/V_0. The variation in V/V_0 with temperature is estimated for spherical nanoparticles, nanowires and nanofilms. It is found that the volume thermal expansivity decreases as size of the nanomaterial increases, whereas V/V_0 increases with temperature across nanomaterials of different sizes. The lattice parameter variation with temperature is studied in Zn nanowires, Se and Ag nanoparticles. It is found that lattice constant increases with increase in temperature. Also, bulk modulus is found to increase with temperature in nanomaterials. The results obtained from the present model are compared with the available experimental data. A good consistency between the compared results confirms the suitability of the present model for studying thermal properties of the nanomaterials.

Keywords. Nanomaterials; shape factor; size effect; thermal expansion; equation of state.

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1. Introduction

The study based on thermophysical, optical, electronic and thermal properties of nanomaterials is of great scientific interest because of their technological applications all over the world [1–4]. However, it is difficult to study such properties as they vary with shape and size of the material. It is noted that the surface area to volume ratios in nanomaterials increase as the size reduces and therefore the thermophysical properties of nanomaterials are different from that of their bulk material. Because of the surface effects, nanomaterials possess more rich metastable structures than their bulk form [5–8]. Also, the number of surface atoms vary with shape of the nanostructure which in turn affects the physical properties of the nanomaterial. Elastic properties like thermal expansivity, lattice parameter, Young's modulus, bulk modulus and volume compression get affected due to change in shape and size of the nanomaterial. The grain size is found to increase with increase in temperature in nanomaterials. Therefore, it is essential to consider both shape and size parameters for understanding the properties of nanomaterials. Various simulations and experimental methods have been described to explore the physical properties of nanomaterials of different sizes [9–12]. Top-down approaches are mostly based on classical thermodynamics and bottom-up approaches are based on complicated simulations for the analysis of thermophysical properties of nanomaterials. Both bottom-up [13,14] and top-down approaches [15,16] are used to study elastic properties of nanomaterials of different shapes at different temperatures. Different theoretical models and equations (EoS) are proposed earlier [17–19] to explore the properties of nanomaterials under pressure and temperature. In the present work, we have proposed a simple and generalised form of EoS to analyse the effect of size, shape and temperature on thermomechanical properties of nanostructures. In the present study, an equation of state is proposed to analyse the effect of shape and size on the volume of nanomaterials at different temperatures. The model theory of formulation is presented in §2 and the validity of the

present approach is discussed in §3 by comparing the calculated results with experimental data.

2. Mathematical formulations

The pressure-dependent equation of state formulated by Goyal and Gupta [20] at room temperature T_0 is as follows:

$$P(V,T_0)=B_0\left(\frac{V_0}{V}-1\right)+B_0\frac{\left(B_0'-1\right)}{2}\left(\frac{V_0}{V}-1\right)^2, \tag{1}$$

where V_0 is the initial volume at room temperature, V/V_0 is the volume compression, B_0 is the bulk modulus at zero pressure and B_0' is its first pressure derivative.

On differentiating eq. (1) with respect to volume V, bulk modulus $B=-V\,(\mathrm{d}P/\mathrm{d}V)$ is obtained as follows:

$$B=\frac{V_0}{V}\left[B_0+B_0\left(B_0'-1\right)\left(\frac{V_0}{V}-1\right)\right]. \tag{2}$$

The inverted form of eq. (1) thus obtained is given by [21]

$$\left(\frac{V}{V_0}\right)^{-1}=1+\frac{\left\{B_0^2+2B_0P(V,T_0)\left(B_0'-1\right)\right\}^{1/2}-B_0}{B_0\left(B_0'-1\right)}. \tag{3}$$

To incorporate the thermal effect in eq. (3), thermal pressure term P_{Th} is added as the total pressure $P(V,T)$ acting on the solid at temperature T is given by [22]

$$P(V,T)=P(V,T_0)+P_{\mathrm{Th}}, \tag{4}$$

where

$$P_{\mathrm{Th}}=\alpha_0B_0(T-T_0). \tag{5}$$

Here, α_0 is the volume thermal expansion coefficient at room temperature T_0.

Using eqs (4) and (5) in eq. (3), the equation of state now becomes

$$\left(\frac{V}{V_0}\right)^{-1}=1+\frac{\left\{B_0^2+2B_0(P-P_{\mathrm{Th}})\left(B_0'-1\right)\right\}^{1/2}-B_0}{B_0\left(B_0'-1\right)} \tag{6}$$

or

$$\left(\frac{V}{V_0}\right)^{-1}=1+\frac{\left[B_0^2+2B_0\{P-\alpha_0B_0(T-T_0)\}\left(B_0'-1\right)\right]^{1/2}-B_0}{B_0\left(B_0'-1\right)}. \tag{7}$$

For nanomaterials, α_0 is replaced by α_{N} at room temperature T_0.

At zero pressure, the isobaric EoS for the nanomaterials is obtained as follows:

$$\left(\frac{V}{V_0}\right)^{-1}=1-\frac{1-\left\{1-2\alpha_{\mathrm{N}}(T-T_0)\left(B_0'-1\right)\right\}^{1/2}}{\left(B_0'-1\right)}. \tag{8}$$

In accordance with Qi and Wang model [23], cohesive energy of the solid nanomaterial E_{cn} is related to cohesive energy of bulk E_0 as follows:

$$E_{\mathrm{cn}}=E_0\left(1-\frac{3N}{4n}\right), \tag{9}$$

where n represents the total number of atoms and N is the number of surface atoms in the nanosolid. As

$$\frac{N}{n}=\frac{\dfrac{\text{Surface area of the nanoparticle}}{\text{Surface area of an atom}}}{\dfrac{\text{Volume of the nanoparticle}}{\text{Volume of an atom}}}$$

or

$$\frac{N}{n}=\alpha\frac{4d}{D}, \tag{10}$$

where D is the diameter of the spherical nanosolid, d is the diameter of an atom of the nanosolid and α is the shape factor defined as [24]

$$\alpha = \frac{\text{Surface area of the non-spherical nanoparticle}}{\text{Surface area of the spherical nanoparticle}}, \tag{11}$$

for the spherical nanoparticle $\alpha = 1$.

So, for the spherical nanosolids having diameter D and diameter of an atom d [24],

$$\frac{N}{2n} = \frac{2d}{D}. \tag{12}$$

For nanowires of diameter D, length L and diameter of an atom of the nanosolid as d [24]

$$\frac{N}{2n} = \frac{2d}{3}\left(\frac{2}{D} + \frac{1}{L}\right).$$

For infinite length of nanowires $L \gg D$, and neglecting the second term, we get

$$\frac{N}{2n} = \frac{4d}{3D}. \tag{13}$$

For nanofilms of diameter L, height h and atomic diameter of the nanosolid as d [24]

$$\frac{N}{2n} = \frac{2d}{3}\left(\frac{2}{L} + \frac{1}{h}\right).$$

As $L \gg h$, neglecting the first term, we get

$$\frac{N}{2n} = \frac{2d}{3h}. \tag{14}$$

As bulk modulus varies linearly with cohesive energy [25], in accordance with eq. (9), bulk modulus of the nanomaterial B_N and that of bulk B_0 are related as follows:

$$B_N = B_0\left(1 - \frac{3N}{4n}\right). \tag{15}$$

Using quasiharmonic approximation [25]

$$\alpha_N B_N = \alpha_0 B_0, \tag{16}$$

where α_0 and α_N are the thermal expansion coefficient of the bulk and nanoform of the material at room temperature T_0.

From eqs (15) and (16),

$$\alpha_N = \alpha_0\left(1 - \frac{3N}{2n}\right)^{-1}. \tag{17}$$

Using eq. (17) in eq. (8), the volume expansion in the nanosolids with temperature, shape and size is given by the relation:

$$\left(\frac{V}{V_0}\right)^{-1} = 1 - \frac{1 - \left\{1 - 2\alpha_0\left(1 - \frac{3N}{4n}\right)^{-1}(T - T_0)\left(B_0' - 1\right)\right\}^{1/2}}{\left(B_0' - 1\right)}. \tag{18}$$

Using eq. (12) in eq. (18), variation in V/V_0 with temperature in the spherical nanosolids is given by

$$\left(\frac{V}{V_0}\right)^{-1} = 1 - \frac{1 - \left\{1 - 2\alpha_0\left(1 - \frac{3d}{D}\right)^{-1}(T - T_0)\left(B_0' - 1\right)\right\}^{1/2}}{\left(B_0' - 1\right)}. \tag{19}$$

Using eq. (13) in eq. (18), variation of V/V_0 with temperature in the nanowires is given by

$$\left(\frac{V}{V_0}\right)^{-1} = 1 - \frac{1 - \left\{1 - 2\alpha_0\left(1 - \frac{2d}{D}\right)^{-1}(T - T_0)\left(B_0' - 1\right)\right\}^{1/2}}{\left(B_0' - 1\right)}. \tag{20}$$

Using eq. (14) in eq. (18), variation of V/V_0 with temperature in nanofilms is given by

$$\left(\frac{V}{V_0}\right)^{-1} = 1 - \frac{1 - \left\{1 - 2\alpha_0\left(1 - \frac{d}{h}\right)^{-1}(T - T_0)\left(B_0' - 1\right)\right\}^{1/2}}{\left(B_0' - 1\right)}. \tag{21}$$

Considering a as the lattice parameter, a/a_0, the lattice parameter variation in nanomaterials, can be obtained using eq. (18) as follows:

$$\frac{a}{a_0} = \left(\frac{V}{V_0}\right)^{1/3} = \left[1 - \frac{1 - \left\{1 - 2\alpha_0\left(1 - \frac{3N}{4n}\right)^{-1}(T - T_0)\left(B_0' - 1\right)\right\}^{1/2}}{\left(B_0' - 1\right)}\right]^{-1/3}. \tag{22}$$

Using eqs (12)–(14) in eq. (22), the lattice parameter variation in spherical nanosolids, nanowires and nanofilms can be obtained.

Considering $(V_0/V) = X$ in eq. (18), the expression for the bulk modulus is obtained in terms of particle size and temperature as follows:

$$B = B_0 X\left\{1 + \left(B_0' - 1\right)(X - 1)\right\}. \tag{23}$$

The expressions of bulk modulus with temperature for spherical nanosolids, nanowires and nanofilms are obtained as follows:

$$B = B_0\left(1 - \frac{1 - \left\{1 - 2\alpha_0\left(1 - \frac{3d}{D}\right)^{-1}(T - T_0)\left(B_0' - 1\right)\right\}^{1/2}}{\left(B_0' - 1\right)}\right) \times \left\{1 - \left(B_0' - 1\right)\left(\frac{1 - \left\{1 - 2\alpha_0\left(1 - \frac{3d}{D}\right)^{-1}(T - T_0)\left(B_0' - 1\right)\right\}^{1/2}}{\left(B_0' - 1\right)}\right)\right\}, \tag{24}$$

$$B = B_0\left(1 - \frac{1 - \left\{1 - 2\alpha_0\left(1 - \frac{2d}{D}\right)^{-1}(T - T_0)\left(B_0' - 1\right)\right\}^{1/2}}{\left(B_0' - 1\right)}\right) \times \left\{1 - \left(B_0' - 1\right)\left(\frac{1 - \left\{1 - 2\alpha_0\left(1 - \frac{2d}{D}\right)^{-1}(T - T_0)\left(B_0' - 1\right)\right\}^{1/2}}{\left(B_0' - 1\right)}\right)\right\}, \tag{25}$$

$$B = B_0\left(1 - \frac{1 - \left\{1 - 2\alpha_0\left(1 - \frac{d}{h}\right)^{-1}(T - T_0)\left(B_0' - 1\right)\right\}^{1/2}}{\left(B_0' - 1\right)}\right) \times \left\{1 - \left(B_0' - 1\right)\left(\frac{1 - \left\{1 - 2\alpha_0\left(1 - \frac{d}{h}\right)^{-1}(T - T_0)\left(B_0' - 1\right)\right\}^{1/2}}{\left(B_0' - 1\right)}\right)\right\}. \tag{26}$$

Table 1. Input parameters [15,16,19].

S. no.	Metallic nanoparticles	d (nm)	$\alpha_0(10^{-5}\mathrm{K}^{-1})$
1	Se [15]	0.4366	9.45
2	Cu [16]	0.256	1.50
3	Pb [19]	0.350	8.7
4	Sn [15]	0.372	2.2

3. Results and discussion

The model proposed here requires the input values of atomic diameter d and volume thermal expansion coefficient α_0 for the bulk material. In the present work, B_0' is approximated as 4 and size of the nanomaterial is considered to be less than 100 nm. The input data required for the calculations are listed in table 1. Equation (17) is used to study the effect of grain size on volume thermal expansion coefficient in spherical nanomaterials, nanowires and nanofilms of Se, Cu and Pb. The results so obtained are shown in figures 1a–1c.

The experimental data available for spherical nanosolid of Se, Cu and Pb are depicted in figures 1a, 1b and 1c along with the present calculated results. It is noted from figure 1 that the volume thermal expansivity increases as the size of the nanomaterial decreases. The experimental values available for volume thermal expansion coefficient with grain size for Se are found to be in close agreement with the calculated results as shown in figure 1a. The experimental values of linear thermal expansion coefficient α_L for bulk Pb is $29 \times 10^{-6}\ \mathrm{K}^{-1}$ [19,26], and so the volume thermal expansion coefficient is considered three times of α_L as a first-order approximation. The volume thermal expansion for Pb nanocrystal (40 nm) is in close agreement with the experimental data; however, the results calculated for 16 nm Pb nanocrystal are largely deviated from the experimental data which may be due to first-order approximation [26]. The trend of variation of thermal expansivity with temperature is found to be the same in Se and Cu nanomaterials. It is also noted that increase in thermal expansion coefficient is more significant in spherical nanosolid for particle size less than 30 nm than

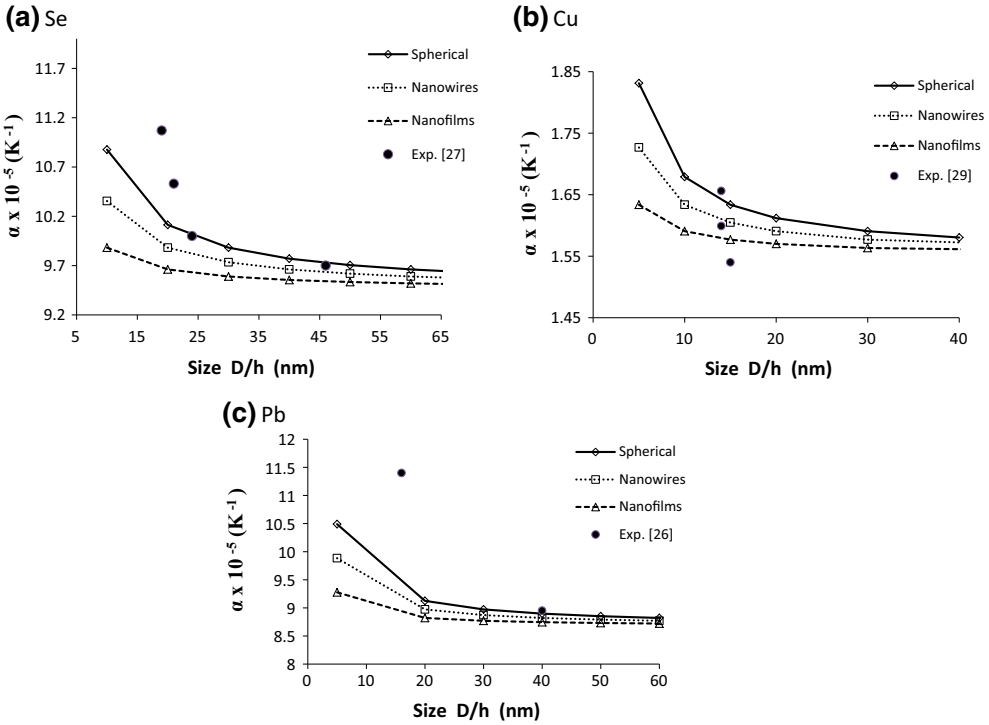

Figure 1. Variation of volume thermal expansivity with size (D/h) nm. D is the diameter of the spherical nanocrystal and nanowire, h represents height of the nanofilm.

in nanowires and nanofilms. However, the increment in thermal expansion coefficient with particle size is least in nanofilms. Therefore, it can be stated that the particle size and shape affect the thermal properties of nanomaterials; specially when the size is less than 30 nm. This is probably due to the increase in surface area to volume ratio with decrease in size in nanosolids.

Equations (19)–(21) are applied to study the variation of V/V_0 with respect to temperature in spherical nanomaterials, nanowires and nanofilms of Se (13 nm), Se (19 nm), Se (21 nm), Se (24 nm), Se (46 nm), Sn (5 nm) and Sn (30 nm). In figures 2a–2e, the theoretical results obtained for V/V_0 with respect to temperature for spherical nanosolid of Se of different sizes are shown along with the available experimental data. The results thus obtained are depicted in figures 2a–2f along with the available experimental data. Increase in V/V_0 with increase in temperature is noticed in spherical nanomaterials, nanowires and nanofilms of the considered nanomaterials. This is due to the thermal expansion in the crystal lattice with increase in temperature, as in general, materials expand on heating. It is clear from the results shown in figures 2a–2f that the increase in V/V_0 with temperature is the most significant in spherical nanosolid and least significant in nanofilms. The variation of V/V_0 with temperature in Sn (5 nm) and Sn (30 nm) is shown in figure 2f. It is clear from the figure that the shape effect neutralises if the grain size of the nanostructure is more than 30 nm. As the size of the nanomaterial increases to 30 nm in the case of Sn nanostructures, the values obtained for the volume expansion at different temperatures in Sn spherical nanoparticle, nanowires and nanofilms are found to almost coincide with each other. However, for particle size less than 30 nm, volume expansion shows considerable change with change in shape of the material.

Further, the variation in lattice parameter with temperature in nanomaterials is studied using eq. (22). The value of volume thermal expansivity for the spherical nanocrystal of Ag is taken as 1.8×10^{-5} K^{-1} [17] and linear thermal coefficient for Zn nanowires is taken as 5.4×10^{-6} K^{-1} [12]. The experimental values of linear thermal expansion coefficient α_{L} for Zn nanowires are available in [12] and hence, volume thermal expansion coefficient is considered to be three times α_{L} as a first-order approximation. The variation in lattice constant with temperature is studied in Zn nanowires (40 nm), Se and Ag nanoparticles. It is found that lattice constant increases with increase in temperature. The computed values of a/a_0 varying with temperature are found to be in close agreement with the available experimental data depicted in figures 3a–3c. The variation of thermoelastic

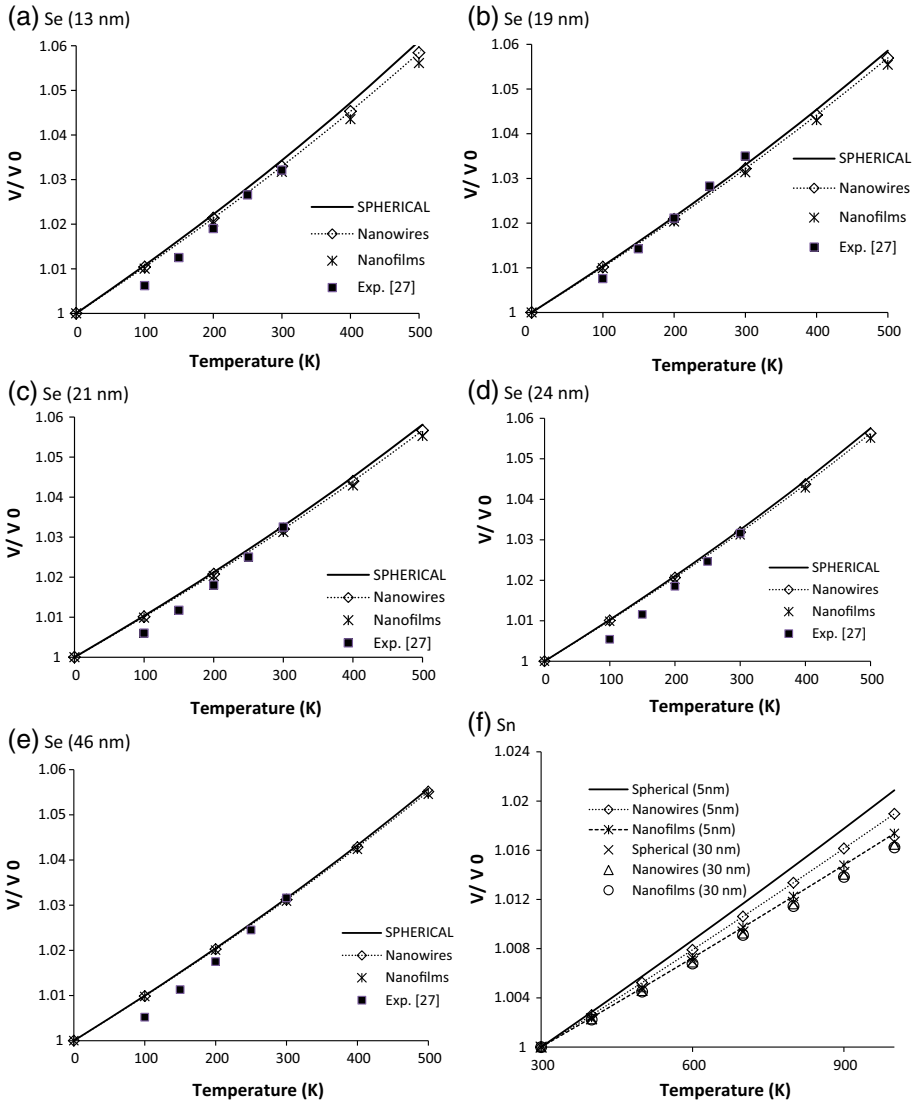

Figure 2. Variation of V/V_0 with temperature in Se and Sn nanostructures.

parameters in nanomaterials is due to decrease in cohesive energy in nanomaterials owing to the increase in surface area to volume ratio.

Equations (24)–(26) are used to find the variation of B/B_0 with temperature in spherical nanomaterials, nanowires and nanofilms of Sn of 5 nm and 30 nm. The results thus obtained are depicted in figures 4a and 4b. It is noted from the figures that the bulk modulus increases with increase in temperature in nanomaterials of different shapes and increase is maximum in spherical nanoparticles with increase in temperature. For particles of size less than 30 nm, shape parameter plays a dominant role as it is observed that thermal expansivity and bulk modulus vary with shape (spherical, nanowires, nanofilms) as well as with size ($<$ 30nm) and show significant deviation in thermoelastic parameters, i.e. more than 10% as is clear from the results depicted in figures 1a–1c, 2g, 4a and 4b. However, for a particle whose size is more than 30 nm, effect of shape is not much significant as the variation in volume expansion and bulk modulus corresponding to different shapes is negligible, i.e. less than 10% as shown in figures.

4. Conclusion

The equation of state used in the present study explains successfully the dependence of temperature, size and shape on volume expansion, lattice parameter and bulk modulus in nanostructures. It can be concluded here that

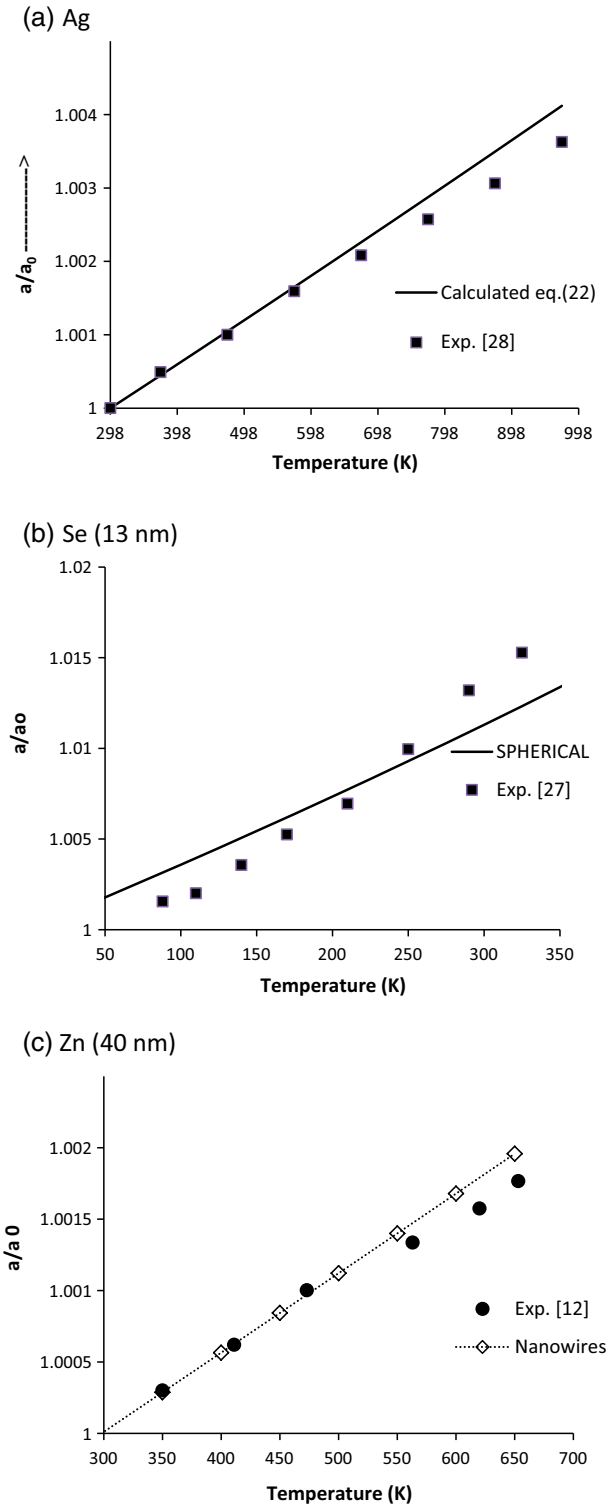

Figure 3. Variation of a/a_0 with temperature in Ag nanoparticles, Se (13 nm) and Zn (40 nm) nanowires.

the volume expansion and lattice parameter of nanomaterials with different shapes and sizes increase with temperature due to increment in surface energy.

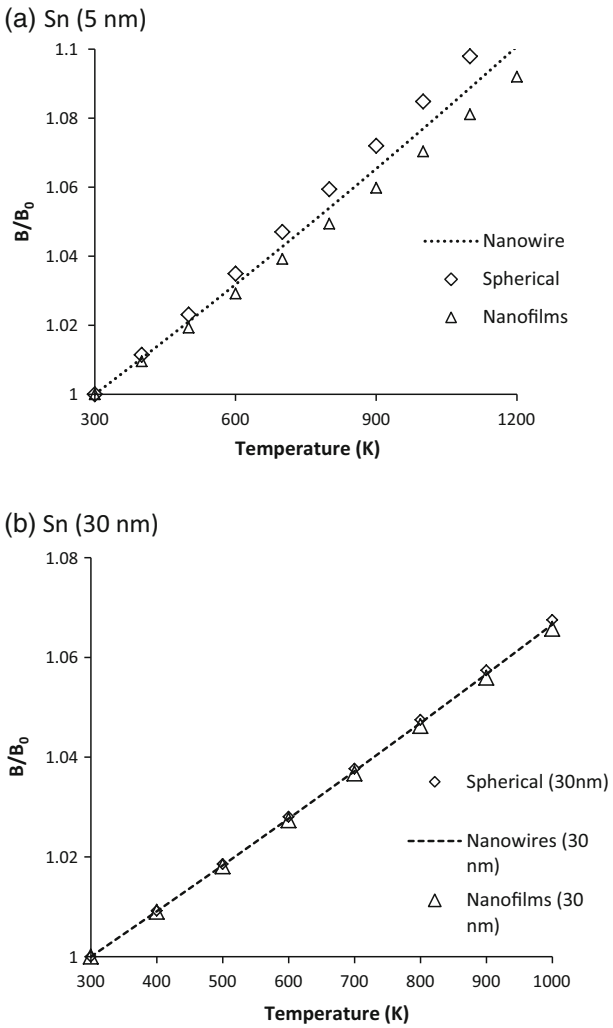

Figure 4. Variation of B/B_0 with temperature in Sn nanostructures.

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