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Grain-size effects on the thermal conductivity of nanosolids

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Abstract

A theoretical model has been developed for the calculation of the thermal conductivity of nanomaterials with different shapes, such as spherical nanosolids, nanowires and nanofilms, based on size-dependent atomic cohesive energy. Thermal conductivity of nanosolids with different shapes decreased as the grain size decreased. The obtained results are compared with the available experimental data. A close agreement between theory and experiment confirmed the validity of the discussed method.

Keywords: Nanomaterials; Thermal conductivity; Surface properties; Shape effect

1. Introduction

Nanomaterials are the foundation of nanoscience and nanotechnology. The idea of nanotechnology was discussed for the first time in the famous talk titled "There is plenty of room at the bottom" given by Richard Feynman at the American Physical Society meeting on December 29, 1959, at Caltech. Nanostructured science and technology is a wide and interdisciplinary area of research and development that has been nurtured worldwide in the past few years. Nanomaterials are exciting because they exhibit strong shape and size effects that cannot be explained by typically theories. Nanocrystals have large surface-to-volume ratios, and surface effects take on a significance that is normally insignificant for bulk materials. Nanoscale Au and Ag exhibit many interesting chemical and physical properties that cannot be observed with their bulk counterparts [1–3]. Liu et al. [4] developed a model to reconcile the observed size dependence of lattice strain, core level shift and elastic modulus of Au and Ag nanostructures, which is based on Goldschmidt Pauling's rule of bond contraction and its extension to the local bond energy and binding energy density.

Various models, such as surface tension, surface relaxation, surface stress, lattice vibration instability and surface phonon instability, have been developed to understand the unusual behaviours of metallic nanostructures [5–9]. A unified analytical model based on the size dependent elastic modulus and vibrational frequency of nanocrystalline metals, ceramics and semiconductors has been established based on the inherent lattice strain and binding energy changes in nanocrystals [10]. In addition, a theoretical explanation of the size effect of the elastic modulus [11] and volume thermal expansion [12] is related to the surface effect by introducing a surface energy contribution.

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Free surface atoms experience a different local environment than atoms in the bulk of a material. Therefore, the energy associated with these atoms will be different from that of the atoms in the bulk. The extra energy shared with surface atoms is called the surface energy. Surface free energy is typically neglected in conventional continuum mechanics because it is associated with only a few layers of atoms near the surface, and the ratio of the volume occupied by the surface atoms and the total volume of the material of interest is extremely small. The study of size and shape effects on nanomaterials has attracted enormous attention due to their scientific and industrial importance. Thermal conductivity is a fundamental property of nanosolids, which directly affects its application. However, few efforts have been focused on studying thermal conductivity.

In this study, based on surface effects, we developed a new model to calculate the thermal conductivity of Si, GaAs, Sn, Ag, and Au and In nanomaterials (i.e., spherical nanosolids, nanofilms and nanowires) based on the size dependent atomic cohesive energy. The model predictions agree well with the available experimental results.

2. Method of analysis

The sum of energy due to the contributions of the interior atoms and the surface atoms of the nanomaterials is defined as the cohesive energy, which is expressed as [13]

$$E_{sum} = E_0(n - N) + \frac{1}{2}E_0 N \tag{1}$$

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

Therefore, $(n-N)$ is the total number of interiors atoms in the nanomaterials. E_0 is the cohesive energy of the bulk material per atom. Eq. (1) may be written as

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

where E_p is the cohesive energy per mole of nanomaterial, which is given by AE_{sum}/n, where A is Avogadro's number. E_b is defined as the cohesive energy per mole of the corresponding bulk material, which is given by $E_b = AE_0$.

Qi [13] reported the relationship between the melting point of nanomaterials and the bulk as

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

The thermal conductivity (k) of bulk materials is expressed as [14]

$$k_b = \left(\frac{1}{3}\right) c v_b l_b, \tag{3}$$

where c is the specific heat, v_b is the average phonon velocity and l_b is the mean free path. The thermal conductivity [15,16] depends on the specific heat, average phonon velocity and mean free path. At room temperature, we assumed that the specific heat is constant. We considered the size dependence of v_p and l_p on the thermal conductivity of the nanomaterials.

The thermal conductivity of nanomaterial can be expressed as

$$k_p = \left(\frac{1}{3}\right) c v_p l_p \tag{4}$$

By combining (3) and (4), we obtained the following relationship

$$\frac{k_p}{k_b} = \left(\frac{v_p l_p}{v_b l_b}\right) \tag{5}$$

The Debye temperature is proportional to the average phonon velocity of the crystal [17], which can be expressed as

$$\theta_b \propto \frac{2h}{\pi k_B}\left(\frac{3N_A}{4\pi V}\right)^{1/3} v_b \tag{6}$$

Similarly, for nanomaterials, the expression is

$$\theta_p \propto \frac{2h}{\pi k_B}\left(\frac{3N_A}{4\pi V}\right)^{1/3} v_p \tag{7}$$

where h is Planck's constant, N_A is Avogadro's number, k_B is Boltzmann's constant, and V is the molar volume.

By combining Eqs. (6) and (7), the following relationship is obtained

$$\frac{v_p}{v_b} = \frac{\theta_p}{\theta_b} \tag{8}$$

The relationship between the melting point and the Debye temperature can be obtained from the Lindemann's proportional. According to this theory, a crystal will melt when the root mean square displacement of an atom exceeds a certain fraction of the interatomic distance in the crystal [18]. By combining specific heat theory with Lindemann's melting formula, the characteristic temperature square is proportional to the melting point of the crystal. Therefore, the Debye temperature of the bulk material can be written as [19]

$$\theta_b^2 \propto \left(\frac{T_b}{MV^{2/3}}\right), \tag{9}$$