

# Effect of Phonon Frequencies on Specific Heat of ZnO Nanostructures

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**Abstract:** The temperature dependent specific heat  $C_p$  of ZnO nanostructures is studied using phonon frequency mechanism. Softening of phonon frequencies at interfaces in nanostructures is considered as the main reason of enhancement in  $C_p$ . Phonon specific heat is estimated using the Debye model which is obtained following an overlap repulsive potential. In nanostructures, having large interface volume ratio, the phonon frequencies and Debye temperature are less at the interfaces than at the core of nanocrystal. The contributions to specific heat due to atoms present at interfaces ( $C^{IF}$ ) and atoms present at the core of nanostructure ( $C^{NC}$ ) are estimated separately by estimating the characteristic Debye temperature ( $\theta_D$ ) using elastic force constant ( $\kappa$ ) to find the total phonon contribution. The temperature derivative of the internal energy yields the electronic contribution to specific heat ( $C_{ei}$ ).

Keywords: Specific heat; Debye temperature; phonons.

## INTRODUCTION

Nanocrystalline (NC) materials are currently a focus of intense investigations because of their temperature and size dependent thermal and electrical properties [1-6]. Nano-crystallization has evolved as a best technique to tune the physical properties those have technological importance [7, 8]. The specific heat capacity  $C_p$  of several nanocrystalline materials observed higher than those observed for their corresponding bulk or crystalline forms [9, 10]. The quantum confinement effects seem to have strong influence on the thermodynamic properties in low dimensional systems [11, 12]. Yet, the fundamental reasons for how and why nano-crystallization enhances the thermodynamic properties are not fully understood.

In recent years, much attention has been paid to the preparation and characterization of one-dimensional (1D) nanomaterials because of their great potential to test fundamental quantum mechanic concepts [13, 14]. In many applications, the sensitivity or efficiency is proportional to the surface area, nanorods or nanowires offer a larger surface area per unit mass compared to that of films or the bulk material. Nanorods or nanowires also offer the opportunity to study the physical properties of one-dimensional structures. Zinc oxide with hexagonal structure belongs to  $C_{6v}^4$  space group. The Raman peaks at 378 and 437  $\text{cm}^{-1}$  are attributed to the A1 mode and the E2 mode of ZnO, respectively. The broadening asymmetry Raman peak at 437  $\text{cm}^{-1}$  is typical of ZnO Raman active branches, which is also one of the characteristics of ZnO nanoparticles [15]. The Raman spectrum of ZnO nanorods is similar to that of nanowires.

As the specific heat of a material is directly related to the atomic structure, investigation of the specific heat as a function of temperature of nanocrystalline (NC) materials should reveal differences in comparison to glassy or crystalline materials of comparable chemical composition. Therefore, for better understanding of the phenomena under investigation, the specific heat of ZnO nanostructures is investigated. From the above results it seems that the change in Debye temperatures ( $\theta_D$ ) at nano level is a possible reason for increase in specific heat  $C_p$ .

## THE MODEL

The acoustic mode frequency shall be estimated in an ionic model using a value of effective ion charge  $Ze$ . The Coulomb interactions among the adjacent ions in an ionic crystal in terms of inverse-power overlap repulsion is presented as [16]

$$\Phi(r) = -(Ze)^2 \left[ \frac{1}{r} - \frac{f}{r^s} \right], \quad (1)$$

here,  $f$  being the repulsion force parameter between two ion cores. The elastic force constant  $\kappa$  is derived from overlap repulsion  $\Phi(r)$  at the equilibrium inter ionic distance  $r_0$  as follows

$$\kappa = \left( \frac{\partial^2 \Phi}{\partial r^2} \right)_{r_0} = (Ze)^2 \left[ \frac{s-1}{r_0^3} \right]. \quad (2)$$

Here,  $s$  is the index number associated with the overlap repulsive potential. The acoustic phonon frequency in terms of atomic mass  $M$  and elastic force constant  $\kappa$  is presented as

$$\begin{aligned} \omega_D &= \sqrt{\frac{2\kappa}{M}}, \\ &= 2(Ze) \sqrt{\frac{(s-1)}{M} \frac{1}{r_0^3}}. \end{aligned} \quad (3)$$

According to Debye theory the specific heat capacity is dominated by the phonons i.e. quantized lattice vibrations and can be estimated using Debye temperature  $\theta_D (= \hbar\omega_D/k_B)$  as a characteristic parameter. The internal energy of the crystal, when the maximum energy of the phonons in the crystal  $x = \hbar\omega/k_B T$ , where phonons frequencies ranging between  $0 < \omega < \omega_m$  (here  $\omega_m$  is maximum phonon frequency which could propagate through crystal)

$$U = U_0 + 9Nk_B T \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3}{(e^x - 1)} dx, \quad (4)$$

The lattice contribution to specific heat capacity can be derived by differentiating above equation with respect to temperature

$$C_{Ph} = 9Nk_B \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (5)$$

with  $\theta_D$  as the Debye temperature and  $N$  is the number of atoms in a unit cell.

In nanostructures, high interfaces volume fraction ratio is observed. At the interfaces density of atoms is comparatively less than the density of atoms in the core of nanocrystals. Also at interfaces inter-atomic distance  $r_0$  is higher than that at the core of nanocrystal, which cause in decrease in the effective Debye frequency (equation 3) and softening of the phonon vibration modes at the interfaces takes place.

In view of nanostructures, the phonon specific heat can be conveniently divided in two parts: the first part represents the specific heat at the interfaces ( $C_{ph}^{IF}$ ) and the second part is the specific heat at the core of nanocrystal ( $C_{ph}^{NC}$ ).

$$C_{Ph} = A_{IF} C_{ph}^{IF} + A_{NC} C_{ph}^{NC} \quad (6)$$

Here,  $A_{IF}$  represents the volume fractional ratio of interfaces in the nanomaterials, and related with the size of nanoparticles, whereas,  $A_{NC}$  is related with  $A_{IF}$  (as  $A_{NC} + A_{IF} = 1$ ).  $C_{ph}^{IF}$  and  $C_{ph}^{NC}$  are function of Debye Temperature at interfaces  $\theta_D^{IF}$  and in the core of nanocrystal  $\theta_D^{NC}$ , respectively. The estimation of electronic contribution to specific heat is described in the following section.

The temperature derivative of the internal energy yields the electronic contribution to specific heat and is expressed as [17]

$$C_{el} = \frac{\pi^2}{3} k_B^2 N(E_F) T = \gamma T \quad (7)$$

here,  $N(E_F)$  represents the density of state at Fermi level and  $\gamma$  denotes the Sommerfield constant. Above equation shows that the electron contribution to specific heat depends on the density of states which is influenced by the effective mass of the carriers and by the carrier concentration.

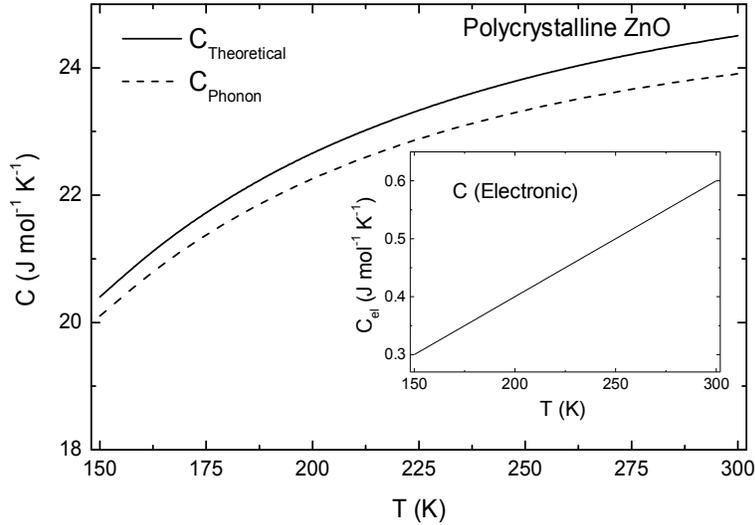
Henceforth, the total specific heat is calculated as sum of lattice contribution and electronic contribution

$$\begin{aligned} C_p &= C_{ph} + C_{el} \\ &= A_{IF} C_{ph}^{IF} + A_{NC} C_{ph}^{NC} + \gamma T \end{aligned} \quad (8)$$

The phonon contribution  $C_{ph}$  varies as  $\beta T^3$ , and follows the Debye  $T^3$  law at low temperatures, here the coefficient  $\beta$  is related to the Debye Temperature  $\theta_D$ . On the other hand, the fermionic contribution  $C_{el}$  ( $=\gamma T$ ) is linear with temperature, the linearity coefficient ( $\gamma$ ) is related to the density of states at the Fermi surface.

## RESULTS AND DISCUSSION

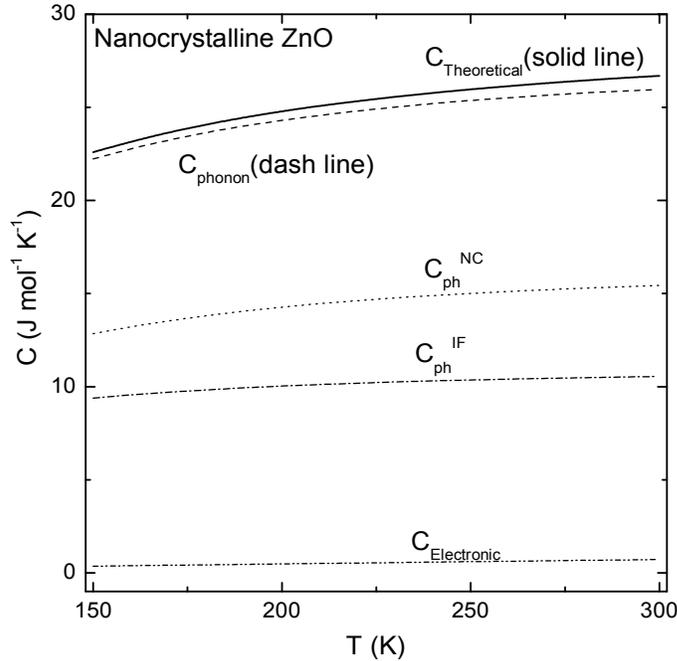
The specific heat capacity ( $C$ ) of polycrystalline and nanocrystalline ZnO are estimated and compared. In present approach the effect of softening of phonon frequencies at the interfaces in nanocrystalline structures on the specific heat is estimated using Debye approach, the contribution due to phonons at the core of nanocrystal as well as at the interfaces along with electronic contribution to specific heat is estimated. The phonon contribution to specific heat  $C_{ph}$  is calculated and plotted in figure 1 (shown by dashed line). Electronic contribution to specific heat is shown in the inset of figure 1. The electronic contribution to specific heat  $C_{el}$  exhibits linear temperature dependence ( $C_{el} = \gamma T$ ).



**Figure 1.** Variation of specific heat  $C$  of polycrystalline ZnO with temperature  $T$ , phonon contribution to  $C$  is represented by dashed line. Inset of figure shows linear temperature dependence of electronic contribution to specific heat.

Nanocrystalline materials consist of two-components: one is nanocrystallites and other is grain boundaries or interfaces components. In nanocrystalline materials, at the interfaces where the interatomic distance is comparatively larger than the lattice parameter, the phonon frequencies decreases and comparatively low  $\theta_D$  is observed at interfaces than  $\theta_D$  at core of nanocrystal. It is to be noticed that the  $\theta_D$  is related with  $r_0$  by equation (3). Further, in nanostructures, at the interface of a nanocrystalline material, resulting in a reduction of  $\theta_D$ , can also be viewed as a softening of force constants ( $\kappa$ ) which measures the strength of interatomic bonds at the grain boundary. This feature of softening of phonon frequencies at the interfaces significantly affects the specific heat. Therefore, in view

of nanostructures, where large interfaces volume fraction ratio is observed, the phonon specific heat is calculated in two parts, representing specific heat at the interfaces and specific heat at the core of nanocrystal. The total phonon specific heat is calculated from equation (6).



**Figure 2.** Variation of specific heat  $C$  of nanocrystalline ZnO with temperature  $T$ , contribution to  $C$  by phonons at core of nanocrystal ( $C_{\text{ph}}^{\text{NC}}$ ) and by phonons at interfaces ( $C_{\text{ph}}^{\text{IF}}$ ) are shown separately.

The value of  $A_{\text{IF}}$  can be estimated, with the help of thickness of the grain boundary ( $d$ ) and mean diameter of the nanoparticles ( $D$ ). For spherical nanoparticles,  $A_{\text{IF}}$  is expressed as  $A_{\text{IF}} = 3d/D$ . It is to be mentioned that, a larger fraction of atoms at the interface is expected for the nanoparticles of smaller size. The temperature dependence of  $C^{\text{IF}}$  and  $C^{\text{NC}}$  are obtained and plotted in figure 2. The total specific heat is estimated as sum of both the contributions from phonon and electron, eventually, theoretically calculated specific heat for nanocrystalline ZnO is plotted by solid line.

## CONCLUSIONS

From above results it appears that the softening of phonon frequencies at the interfaces is the main reason for enhancement in specific heat of nanocrystalline materials. The specific heat results revealed that the  $C_p$  of nanocrystalline ZnO is about 10% higher than in the polycrystalline state.

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