

Lattice Thermal Conductivity in Nano- to Micro-scale Porous Materials

ROLAND H. TARKHANYAN, A. IOANNIDOU, and DIMITRIS G. NIARCHOS

We study the effect of thermal phonon scattering on the reduction of lattice thermal conductivity (LTC) in porous materials with spherical pores and inclusions of varying diameters from nano- to microscale sizes. Using a model based on the Gamma distribution of the pore sizes, we calculate effective phonon mean free paths at scattering on randomly distributed pore boundaries and obtain a general relationship in “gray medium” approximation for the LTC of the material. Then, we determine the LTC of multiple phases in the presence of inclusions of various size scales embedded within a single host material and obtain a simple analytic expression for the effective LTC of a three-phase composite with nano- and microscale randomly distributed inclusions. We show that the presence of hollow pores and (or) inclusions with the all-scale hierarchical disorder leads to a considerable reduction in the LTC of the composite. For example, the thermal conductivity of such a composite on the basis of PbTe in some specific cases may possibly be reduced by more than one order of magnitude, which is very useful to achieve a large enhancement in the thermoelectric figure of merit ZT. Results of our model are compared with the existing experimental data.

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I. INTRODUCTION

THERMOELECTRIC materials which can generate electricity from waste heat represent a highly important and dynamic research area that aims at the creation of efficient solid-state energy-conversion devices.^[1–4] In the last two decades, a great effort has been made to enhance the range of composite materials which exhibit higher thermoelectric figure of merit $ZT = \sigma S^2 T / (K_e + K_L)$ (σ —electrical conductivity, S —the Seebeck coefficient, T —temperature, K_e and K_L —the electronic and lattice thermal conductivities, respectively) compared to that in classical bulk semiconductors.^[5–9] As regards the theoretical studies on thermoelectrical properties of complex materials, they have been started since the pioneering works of Rayleigh^[10] and Maxwell-Garnet^[11] who derived expressions for thermal conductivity of a medium with spherical pores, and such studies are still in progress (see, for example,^[12,13]). However, despite the rapid progress in technology of high-performance thermoelectric materials during the last decade, very few experimental and theoretical works have yet been done to analyze the thermal transport properties in

inhomogeneously porous semiconductors in the presence of pores or inclusions of varying size and porosity scales.^[14–17] Recently, the group of Kanatzidis achieved a record high ZT value of ~2.2 at 915 K (642 °C) with the introduction of SrTe nanoscale precipitations ranging from 1 to 17 nm and micrograins ranging from 0.1 to 1 μm in the Na-doped PbTe matrix.^[15] The authors have used a “panoscopic” hierarchical architecture approach for integrated phonon scattering across multiple length scales. It is evident that in this way, more extensive phonon scattering and, consequently, stronger reduction in lattice thermal conductivity (LTC) can be achieved than in the case of nanostructuring alone, and that the main physical reason leading to the enhancement of the thermoelectric figure of merit is the reduction in the LTC.^[17]

The aim of this work is to examine how the presence of randomly distributed hollow pores and (or) inclusions of different size scales can vary the thermal conductivity of porous materials and multiphase composites, aiding in the design of better thermoelectric materials with lower thermal conductivity and higher figure of merit ZT. It is worthy to note that the estimation of thermal conductivity of multiphase systems has been attracting researchers’ interest for more than a century. Kaviany^[18] described the extensive review of the literature on porous media. Using the intensity-based version^[19] of the Boltzmann transport equation, Prasher^[20] develops ballistic-diffusive effective medium model for the transverse thermal conductivity of two-dimensional nanoporous and microporous materials made from aligned cylindrical pores. Recently, Tian *et al.*^[21] applied first-principles calculations to lead telluride, lead selenide, and their alloys ($\text{PbTe}_{1-x}\text{Se}_x$) to investigate phonon

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transport properties and have shown that, besides nanostructuring, alloying may be another relatively effective way to reduce the LTC. He *et al.*^[22] have used the Callaway's model^[23] to determine the thermal conductivity of nanometer-scale structures of PbTe_{0.7}S_{0.3} in spinodal decomposition phase state and found that boundaries, dislocations, and precipitates significantly reduce the LTC of the structures well below that of pure PbTe. However, all these models have limited applicability in real-time experimental situation described in.^[15] The present paper deals with a simplified approach to solve the problem. We apply "gray medium" model, resistor concept and Gamma distribution for both nano- and microscale inclusions to derive an expression for the LTC of real three-phase composite. The model used in our recent work^[16] has been modified in terms of the properties of constituent phases. These modifications lead to better agreement of predicted values with the experimental data presented in Reference 15.

The paper is organized as follows: in the next section, the details of modeling for a porous material with randomly distributed spherical non-overlapping hollow pores are given, and the LTC of such a material is considered on the basis of the Gamma distribution for the pore sizes. In Section III, we derive an analytic expression for the effective LTC of a porous medium with inhomogeneous porosity in the presence of n different groups of empty pores with various size scales. In Section IV, we consider the effective LTC of a multi-layer composite consisting of n alternating layers of the same host material connected thermally in series, with pores of different scales and various porosities. In Sections V and VI, we generalize the obtained results in the case of three-phase composites in which the pores are replaced (or fulfilled) by nano- and microsized inclusions and make a comparison of our predictions with the existing experimental results. Finally, in Section VII, we present concluding remarks.

II. EFFECTIVE LTC OF A POROUS MEDIUM WITH RANDOMLY DISTRIBUTED PORES

Consider a porous medium in the presence of n different groups of non-overlapping spherical hollow pores with various size scales, *e.g.*, nanoscale pores with average diameter \bar{d}_1 and volume fraction (porosity) φ_1 , microscale ones with the average diameter \bar{d}_2 and the porosity φ_2 , etc. Let us introduce nondimensional variables:

$$\rho_i = d_i/\bar{d}_i, \quad i = 1, 2, \dots, n, \quad [1]$$

where d_i are randomly distributed pore diameters around \bar{d}_i . We assume that each of the variables ρ_i is described by probability density function

$$f(\rho_i) = \frac{N(\rho_i)}{N_i} = \frac{\rho_i^{\alpha_i-1} \exp(-\rho_i/\beta_i)}{\beta_i^{\alpha_i} \Gamma(\alpha_i)}, \quad [2]$$

where $N(\rho_i)d\rho_i$ is the no. of pores of the same scale with nondimensional diameters in the interval: $\rho_i, \rho_i + d\rho_i$, N_i is the total no. of the pores in the group; $\alpha_i > 1$ and β_i

are the "shape" and "scale" parameters of the Gamma distribution, respectively;^[24]

$$\Gamma(\alpha_i) = \int_0^\infty x^{\alpha_i-1} e^{-x} dx \quad [3]$$

is the gamma function; and $\bar{\rho}_i$ is the mean (first moment) of the corresponding distribution. By definition (Eq. [1]),

$$\bar{\rho}_i = \int_0^\infty \rho_i f(\rho_i) d\rho_i = \alpha_i \beta_i = 1, \quad [4]$$

so that

$$\beta_i = \alpha_i^{-1}. \quad [5]$$

The variance of the distribution is equal to $\alpha_i \beta_i^2$, using which for the second moment, one can obtain

$$\bar{\rho}_i^2 = \bar{\rho}_i^2 + \alpha_i \beta_i^2 = 1 + \alpha_i^{-1}. \quad [6]$$

Note that if the standard deviation $\alpha_i^{-1/2} \bar{\rho}_i$ is much less than the mean, *i.e.*, when $\sqrt{\alpha_i} \gg 1$, the distribution function $f(\rho_i) \sim \delta(\rho_i - \bar{\rho}_i)$.

The porosity φ_i is proportional to $\bar{\rho}_i^2$:

$$\varphi_i = \frac{\pi \bar{d}_i^3}{2V} \int_0^\infty \rho_i^2 f(\rho_i) d\rho_i, \quad [7]$$

where V is total volume of the sample, and

$$V_i = \pi \bar{d}_i^3 \bar{\rho}_i^2 / 2 \quad [8]$$

is net pore volume of the pores with the same size scale.

Consider first the effective LTC of a porous medium with only one group of pores of the same scale. In the frequency-independent (gray medium) approximation,^[25,26] neglecting dependence of the phonon relaxation times in the bulk material on the phonon energy and considering the phonon-pore-scattering and the bulk-scattering processes as independent events, the LTC can be given by simple expression:^[16]

$$\frac{K_{\text{eff}}}{K_b} = \frac{1 - \varphi}{\Lambda_b / \Lambda_{\text{eff}}}, \quad [9]$$

where K_b and Λ_b are, respectively, the LTC and the average phonon mean free path (MFP) in the bulk material at zero porosity, and Λ_{eff} is the effective phonon MFP in the porous material with average pore diameter \bar{d} . It is evident that the presence of randomly distributed pores leads to a shortening of the MFP of thermal phonons. Assuming that the scattering of phonons on the pores is diffuse and using the Matthiessen rule for isotropic scattering, one can obtain

$$\Lambda_{\text{eff}}^{-1} = \Lambda_b^{-1} + \Lambda_p^{-1}, \quad [10]$$

where Λ_p is the phonon MFP due to scattering at pore/medium interfaces. For the i^{th} group of pores, it can be calculated using the well-known relation:

$$\Lambda_{pi}^{-1} \cong \sigma_i c_i, \quad [11]$$

where σ_i is the effective cross-sectional area for a phonon collisions with the pores,

$$\sigma_i = \frac{\pi}{2} \bar{d}_i^2 \int_0^\infty \rho_i f(\rho_i) d\rho_i = \frac{\pi}{2} \bar{d}_i^2, \quad [12]$$

and $c_i = N_i/V$ is the pore number density (concentration). The no. of the pores of the same scale can be estimated as $N_i \simeq 6V_i/\pi\bar{d}_i^3$, where V_i is the total volume of the pores given by Eq. [8]. Taking into account that

$$\bar{d}_i^3 = \bar{d}_i^3 \int_0^\infty \rho_i^3 f(\rho_i) d\rho_i = \bar{d}_i^3 \beta_i^3 \frac{\Gamma(\alpha_i + 3)}{\Gamma(\alpha_i)} \quad [13]$$

and using Eqs. [6] and [7], one can obtain

$$c_i = \frac{3\bar{d}_i^3 \beta_i^2}{\bar{d}_i^3 V} = \frac{6\varphi_i}{\pi\bar{d}_i^3} \quad [14]$$

and, consequently,

$$\Lambda_{pi} = \frac{\bar{d}_i}{3g(\alpha_i)\varphi_i}, \quad [15]$$

where

$$g(\alpha_i) = \frac{\alpha_i^2}{(\alpha_i + 1)(\alpha_i + 2)}. \quad [16]$$

Note that by introducing a new parameter, interface density S_i , i.e., the surface area per unit volume of the material for each group of the inclusions:

$$S_i = 2\pi c_i \bar{d}_i^2 \int_0^\infty \rho f(\rho) d\rho = 12\varphi_i g(\alpha_i)/\bar{d}_i, \quad [17]$$

the phonon MFP due to scattering at medium/pore interfaces can be presented as

$$\Lambda_{pi} = 4/S_i. \quad [18]$$

Note also that Λ_{pi} coincides with that in a homogeneously porous medium with simple 3D cubic array of identical spherical pores, (Reference 16) only if $g(\alpha_i) = 1/2$, i.e., when the shape parameter α_i of the random pore size distribution is equal to $(3 + \sqrt{17})/2 \approx 3.56$.

Substitution of Eqs. [10] and [15] into [9] gives

$$\frac{K_{eff,i}}{K_b} = \frac{1 - \varphi_i}{1 + 3\varphi_i \Lambda_b g(\alpha_i)/\bar{d}_i}, \quad [19]$$

which means that the effective LTC depends not only on the porosity and average size of the pores but also on the shape parameter of the Gamma distribution: at given values of φ_i and \bar{d}_i , $K_{eff,i}$ decreases monotonically

with the increasing α_i remaining always greater than minimum value:

$$K_{eff,i}^{\min} = \frac{(1 - \varphi_i) K_b}{1 + 3\varphi_i \Lambda_b / \bar{d}_i}. \quad [20]$$

Except that, according to Eq. [19], at a given value of the shape parameter, $K_{eff,i}$ decreases monotonically with the increasing porosity. As regards the dependence on average pore diameter, it has an opposite behavior, i.e., $K_{eff,i}$ increases monotonically with the increasing \bar{d}_i , as has been mentioned already in.^[16]

III. EFFECTIVE LTC OF A POROUS MEDIUM IN THE PRESENCE OF n DIFFERENT GROUPS OF HOLLOW PORES WITH VARIOUS SIZE SCALES

Consider now a porous medium in the presence of n different groups of the pores with porosities: $\varphi_1, \varphi_2, \dots, \varphi_n$ and various size scales around average diameters: $\bar{d}_1, \bar{d}_2, \dots, \bar{d}_n$, respectively. In this case, the effective phonon MFP is given by

$$\Lambda_{eff}^{-1} = \Lambda_b^{-1} + \sum_{i=1}^n \Lambda_i^{-1} \quad [21]$$

and then, using Eqs. [9] and [15], for the ratio of the effective LTC of such a medium to the LTC of the bulk material with zero porosity, we obtain a general expression:

$$\frac{K_{eff}}{K_b} = \frac{1 - \sum_{i=1}^n \varphi_i}{1 + 3\Lambda_b \sum_{i=1}^n \varphi_i g(\alpha_i)/\bar{d}_i}. \quad [22]$$

Using Eq. [22], it is not difficult to conclude that the presence of hollow pores with the all-scale hierarchical disorder leads to a colossal reduction in the LTC. Obviously, such a reduction in the LTC is very desirable for a large enhancement in the thermoelectric figure of merit of thermoelectric materials.

As an example, let us consider a particular case when $n = 2$. Then, Eq. [22] gives

$$\frac{K_{eff}}{K_b} \equiv \frac{K_0}{K_b} = \frac{1 - \varphi_1 - \varphi_2}{1 + 3\Lambda_b [\varphi_1 g(\alpha_1)/\bar{d}_1 + \varphi_2 g(\alpha_2)/\bar{d}_2]} \quad [23a]$$

or, at $\varphi_1 = \varphi_2 \equiv \varphi$,

$$\frac{K_0}{K_b} = \frac{1 - 2\varphi}{1 + 3\Lambda_b \varphi G}, \quad [23b]$$

where

$$G = \frac{g(\alpha_1)}{\bar{d}_1} + \frac{g(\alpha_2)}{\bar{d}_2}. \quad [23c]$$

For estimations, in the following, we will consider two different datasets of the shape parameters: (a) $\alpha_1 = 3.5$,

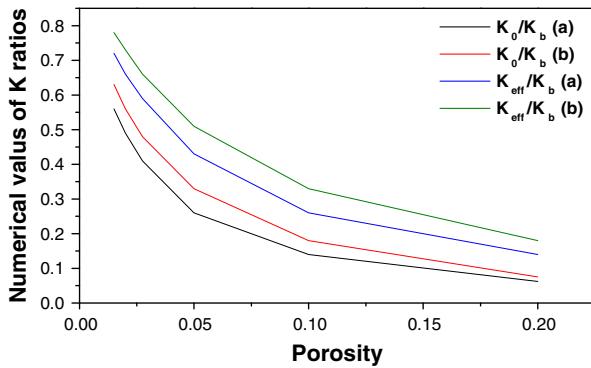


Fig. 1—Numerical values of the ratio K_0/K_b (Eq. [23b]) and K_{eff}/K_b for different porosities and sets of the shape parameters according to Eq. [27b].

$$\frac{K_{\text{eff}}}{K_b} = \frac{(1 - \varphi_1)(1 - \varphi_2)}{1 - (\varphi_1 + \varphi_2)/2 + (3\Lambda_b/2)[\varphi_1 g(x_1)(1 - \varphi_2)\bar{d}_1^{-1} + \varphi_2 g(x_2)(1 - \varphi_1)\bar{d}_2^{-1}]}. \quad [27a]$$

$\alpha_2 = 8$ and (b) $\alpha_1 = 2.259$, $\alpha_2 = 8.335$. Then, substituting in Eq. [23b] $\Lambda_b = 90$ nm at room temperature (PbTe,^[27]) $d_1 = 2.8$ nm, $d_2 = 0.8 \mu\text{m}$, for different values of φ , we obtain the results shown in Figure 1 (two lower curves). Note that for the set (a) at porosities $\varphi_1 = \varphi_2 = 0.2$ the LTC of the porous material decreases about 16 times! It means that in the case of unaffected by pores' power factor, the thermoelectric figure of merit of the material ZT can be increased by more than one order of magnitude.

IV. EFFECTIVE LTC OF A MULTILAYER COMPOSITE CONSISTING OF LAYERS WITH PORES OF DIFFERENT SCALES AND VARIOUS POROSITIES

In the previous section, we have assumed that the pores of different size scales are distributed in the same layer of the thermoelectric material. Consider now briefly a composite consisting of n alternating layers of the same host material with thicknesses: l_i , porosities: φ_i , $i = 1, 2, \dots, n$, and pores of different scales, so that in each layer, there are randomly distributed pores of the same scale, which are described by probability density functions $f(\rho_i)$ given by Eq. [2]. Since the layers are connected thermally in series, the effective thermal conductivity of such a composite with inhomogeneous porosity is given by the relation:^[16]

$$\frac{1}{K_{\text{eff}}} = \frac{1}{L_z} \sum_{i=1}^n \frac{l_i}{K_{\text{eff},i}}, \quad [24]$$

where L_z is the thickness of the composite in the direction parallel to the temperature gradient. From the

experimental point of view, it is convenient to consider the case when a layer thickness $l_i = \text{const}$. Then, from Eqs. [19] into [24], we obtain

$$\frac{K_{\text{eff}}}{K_b} = \frac{1}{1 + \bar{\psi}}, \quad [25]$$

where

$$\bar{\psi} = \frac{1}{n} \sum_{i=1}^n \psi_i, \quad \psi_i = \frac{\varphi_i [1 + 3\Lambda_b g(\alpha_i) \bar{d}_i^{-1}]}{1 - \varphi_i}. \quad [26]$$

The expression (25) is sufficiently sound for applications in a concrete experimental situation. In the case of two-layer composite, it gives

Setting here $\varphi_1 = \varphi_2 \equiv \varphi$, one can obtain a simple relationship:

$$\frac{K_{\text{eff}}}{K_b} = \frac{1 - \varphi}{1 + 3\Lambda_b\varphi G/2}, \quad [27b]$$

where G is given by Eq. [23c]. A comparison of Eqs. [23b] and [27b] shows obviously that the reduction in the LTC of the medium considered in previous section is significantly stronger than that in the multilayer composite. For example, using the same data for estimations indicated according to Eq. [23c], from Eq. [27b], one can obtain the results shown in the same Figure 1. Using the data of the figure, we conclude again that the medium with pores of different size scales in the same host material is more preferable than a multilayered composite different layers of which contain only pores of the same scale. That is why in the following, we will restrict ourselves to the consideration of a medium with inclusions in a single bulk material.

V. THE LTC OF MULTIPLE PHASES EMBEDDED WITHIN A SINGLE BULK MATERIAL

We next consider multiphase composites in which the pores are replaced (or fulfilled) by non-touching inclusions of various size scales. In this case, before attempting to derive a general expression for the effective LTC of the composite, we have to determine thermal conductivities of the inclusions and those of the host phase separately.

Consider first the inclusion phase with volume fraction φ_i and bulk LTC $K_{i,b}$. In the same “gray medium” approximation, the bulk LTC of a macroscopic sample can be expressed as^[25,26]

$$K_{i,b} = \frac{1}{3} C_{i,b} v_i \Lambda_{i,b}, \quad [28]$$

where $C_{i,b}$ is the volumetric specific heat, v_i is the average phonon group velocity, and $\Lambda_{i,b}$ is the average bulk phonon MFP. Let us present the LTC of an inclusion K_i in the form analogous to Eq. [28] and assume that both $C_{i,b}$ and v_i in the inclusions are the same as those in the bulk material. Then, we obtain

$$\frac{K_i}{K_{i,b}} = \frac{\Lambda_i}{\Lambda_{i,b}}. \quad [29]$$

In the case of diffuse scattering of phonons localized inside an inclusion, Λ_i can only depend on the bulk MFP and the characteristic length of the inclusion. Thus, using again the Mathiessen rule, for Λ_i , one can get

$$\frac{1}{\Lambda_i} = \frac{1}{\Lambda_{i,b}} + \frac{1}{d_i}, \quad [30]$$

and, therefore,

$$\frac{K_i}{K_{i,b}} = \frac{1}{1 + \Lambda_{i,b}/d_i}. \quad [31]$$

As regards the thermal conductivity of the host phase, it has been considered already in Section III and coincides with Eq. [22].

VI. EFFECTIVE LTC OF A THREE-PHASE COMPOSITE. COMPARISON WITH EXPERIMENTAL RESULTS

For definiteness and simplicity, furthermore we will restrict ourselves to the consideration of a three-phase composite with only two different groups of inclusions with various size scales, namely, nanoscale ($i = 1$) and microscale ($i = 2$) inclusions. The main component of the composite is the porous matrix (host phase), parameters of which will be indicated by subscript 0.

We will estimate the effective LTC of such a composite K_{eff} on the basis of the thermal-electrical analogy, *i.e.*, considering various components as resistors. Then, assuming perfect interfacial contact between different constituent phases, for the upper and lower bounds of the K_{eff} , one can obtain the following:

$$K_{\max} = (1 - \varphi_1 - \varphi_2)K_0 + \varphi_1 K_1 + \varphi_2 K_2, \quad [32]$$

$$\frac{1}{K_{\min}} = \frac{1 - \varphi_1 - \varphi_2}{K_0} + \frac{\varphi_1}{K_1} + \frac{\varphi_2}{K_2}, \quad [33]$$

which are the weighted arithmetic and harmonic means, respectively. It is clear that the precise value of K_{eff} is between K_{\min} and K_{\max} . We will present K_{eff} as a linear superposition:

$$K_{\text{eff}} = AK_{\min} + BK_{\max}. \quad [34]$$

Using Eqs. [32] to [34] and taking into account that at $\varphi_1 = \varphi_2 = 0$ $K_{\text{eff}} = K_{0b}$, one can obtain

$$A + B = 1. \quad [35]$$

The second equation for the determination of A and B can be found assuming that when $\varphi_1 = \varphi_2 = 1/3$, K_{eff} is equal to the weighted geometric mean f_1 :

$$f_1 = (\bar{K}_0 K_1 K_2)^{1/3}, \quad \bar{K}_0 = \frac{K_b}{3(1 + \Lambda_b G)}. \quad [36a]$$

With this simplifying approximation, one can get

$$A = \chi B, \quad B = (1 + \chi)^{-1}, \quad [36b]$$

where

$$\chi = \frac{f_3(f_2 - f_1)}{f_1(f_3 - f_1)}, \quad [36c]$$

$$f_2 = (\bar{K}_0 + K_1 + K_2)/3, \quad f_3 = [\bar{K}_0(K_1 + K_2) + K_1 K_2]/3. \quad [36d]$$

Finally, for the effective LTC of the three-phase composite, we obtain

$$K_{\text{eff}} = K_{\min} + \frac{K_{\max} - K_{\min}}{1 + \chi} = K_{\max} - \frac{(K_{\max} - K_{\min})\chi}{1 + \chi}, \quad [37]$$

where K_{\min} and K_{\max} are given by Eqs. [32] and [33].

Let us now apply Eq. [37] for an estimation of the LTC in thermoelectric material with multiscale architecture used in the experimental work.^[15] Consider Na-doped PbTe matrix as the host phase and SrTe nanoscale precipitations and microscale grains as inclusions with randomly distributed sizes. Unfortunately, no experimental data exist for the values of the LTC and MFP in bulk SrTe, because of which in the following estimations, we have to assume that these parameters coincide with those in PbTe bulk. In particular, we will use the values at various temperatures, as listed in Table I.

The corresponding results for K_1 (the LTC of nanoscale inclusions) and K_2 (mesoscale grains) are shown in Figure 2, where for the completeness is shown also the temperature dependence of K_{0b} .

Figures 3(a) and (b) show the temperature dependence of the LTC of the host phase $K_0(a)$ and $K_0(b)$ according to Eq. [23b] at various porosities: $\varphi_1 = \varphi_2 = \varphi$ for set (a) of the shape parameters ($\alpha_1 = 3.5$, $\alpha_2 = 8$) and set (b), respectively: ($\alpha_1 = 2.259$, $\alpha_2 = 8.335$). As before, the average diameters of the inclusions are assumed to be $\bar{d}_1 = 2.8 \text{ nm}$, and $\bar{d}_2 = 0.8 \mu\text{m}$.^[15]

Finally, using Eqs. [32], [33], and [37], for the effective LTC at various temperatures in the range from 300 K to 600 K (27 °C to 327 °C), at different porosities and sets of shape parameters (a) and (b), we obtain the results presented in Figures 4(a) and (b).

Table I. The LTC and MFP in Bulk Materials and Inclusions at Various Temperatures

T [K (°C)]	300 (27)	350 (77)	400 (127)	450 (177)	500 (227)	550 (277)	600 (327)
$K_{1,b} = K_{2,b} = K_{0b}$ (Wcm ⁻¹ K ⁻¹)	2.8	2.2	1.8	1.6	1.4	1.2	1.1
$\Lambda_{1,b} = \Lambda_{2,b} = \Lambda_{0b}$ (nm)	90	82	75	68	60	52	45

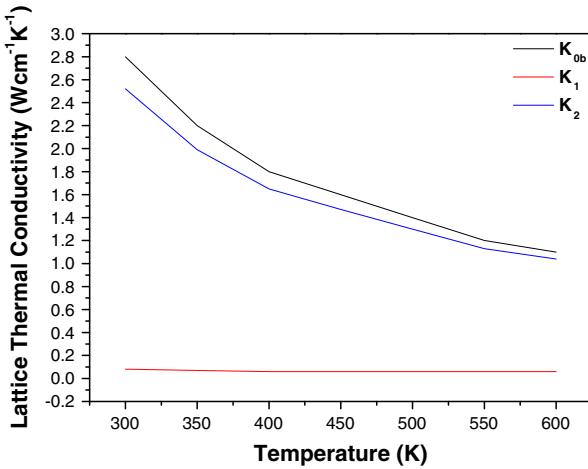
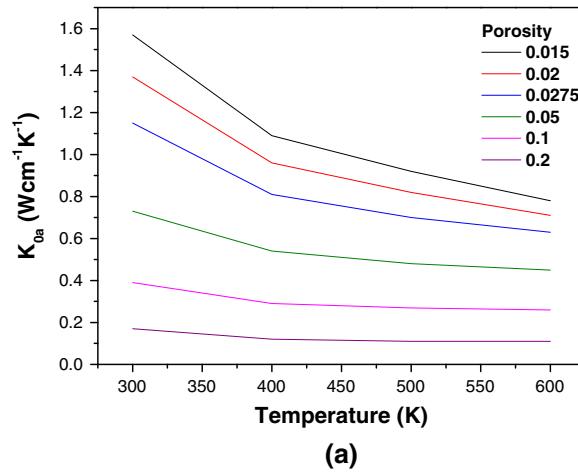


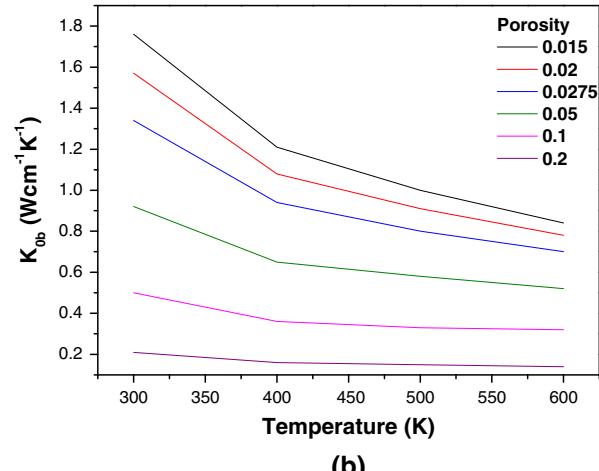
Fig. 2—Temperature dependence of LTC in the bulk and inclusions.

Figure 5 shows a comparison of our results for the effective LTC $K_{\text{eff}}(b)$ with the experimental data reported in.^[15] At set (b) for α and porosity $\varphi = 0.015$, which is the case, our theoretical predictions are in good agreement with experimental values. A small difference between these predictions may be noticed: in particular, due to the slight shifts in the values of the bulk MFP from those shown in Table I; or due to the presence of other peculiarities in experiments and disagreements with the estimated values of the parameters used, such as the deviation of inclusion shape from a sphere, and different values of the LTC in bulk SrTe and PbTe. However, the main conclusion made, based on Figures 4 and 5, is that the effective LTC of three-phase composite material decreases monotonically as temperature or porosity increases, and this result is well confirmed by experimental data of Biswas *et al.*^[15]

Let us also consider briefly a composite containing nanoscale hollow pores and mesoscale particle inclusions. There exist two different ways to obtain such a composite from the three-phase one: (a) by replacing nanoscale inclusions by empty pores, and (b) by assuming that temperature cannot vary within a particle on a scale smaller than average MFP. Really, if a particle size is less than MFP, then one cannot define the temperature $T(z)$ as a function of the coordinate (the z -axis is along the temperature gradient) within this particle, *i.e.*, the whole particle is probably at the same temperature. Since nanoscale precipitations used in^[15] are in the range from 1 to 17 nm, *i.e.*, less than average MFP Λ_{0b} , we may assume that thermal phonons inside nanoscale inclusions practically do not play any role in thermal conductivity, *i.e.*, heat is carried only by phonons of the matrix and by phonons localized in mesoscale grains. In other words, we can consider nano-inclusions as hollow



(a)



(b)

Fig. 3—Temperature dependence of the LTC for the host phase (porous PbTe) of three-phase composite at different porosities and sets (a) and (b) of the shape parameters.

pores and set $K_1 = 0$. Then, Eqs. [32] and [33] should be replaced, respectively, by

$$K_{\max} = (1 - \varphi_1 - \varphi_2)K_0 + \varphi_2K_2, \quad [38]$$

and

$$K_{\min} = \frac{K_0K_2}{\varphi_2K_0 + (1 - \varphi_1 - \varphi_2)K_2}, \quad [39]$$

while χ in Eqs. [36b] and [37] should be replaced by ξ , where

$$\xi = \frac{\xi_2(\xi_2 - \xi_1)}{\xi_1(\xi_2 - \xi_1^2)}, \quad [40]$$

$$\xi_1 = (\bar{K}_0K_2)^{1/3}, \quad \xi_2 = (\bar{K}_0 + K_2)/3. \quad [41]$$

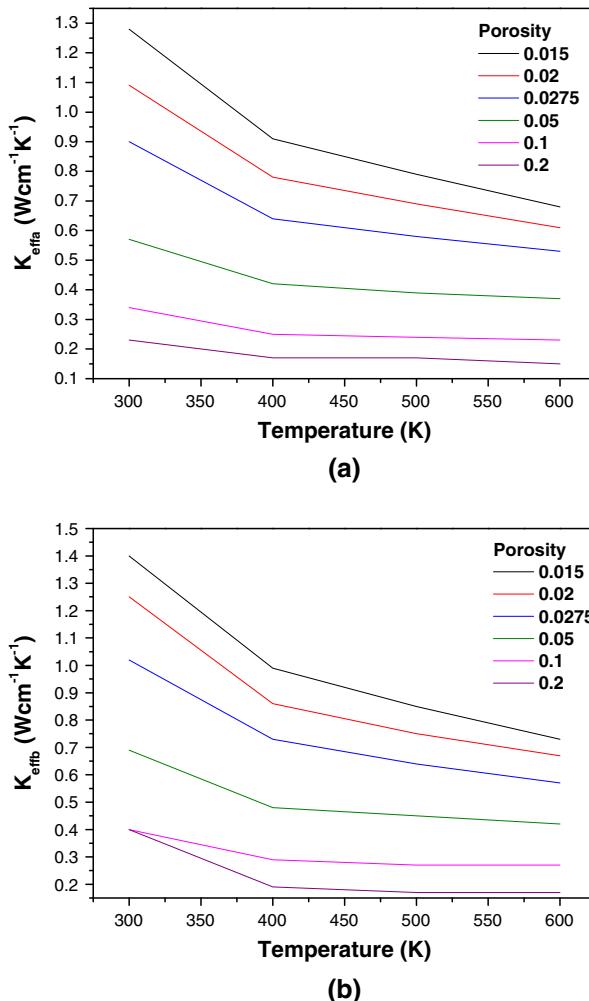


Fig. 4—The effective LTC (K_{eff} , $\text{Wcm}^{-1} \text{K}^{-1}$) according to Eq. [37] at various porosities and temperatures for two different sets (a) and (b) of the shape parameters.

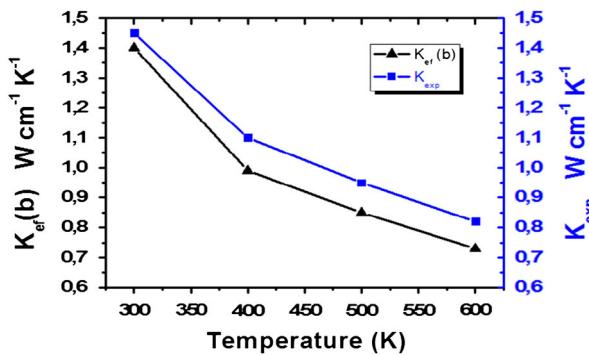


Fig. 5—Comparison of our results for the effective LTC $K_{\text{eff}}(b)$ at porosity $\phi = 0.015$ with experimental data reported in^[15].

Using Eqs. [37] to [41], it is not difficult to see that the effective LTC of the composite with hollow nanoscale pores' and mesoscale particles' inclusions is less compared to that for three-phase material considered at the

beginning of this section, whereas it is greater than that of the porous materials containing the all-scale hollow pores.

VII. CONCLUSIONS

The main results of this paper can be summarized as follows:

1. Using a model based on the Gamma distribution of the pore sizes, a simple and quite general expression is derived for the effective LTC of a three-phase composite consisting of two different groups of inclusions with various size scales, embedded in a single host material.
2. Theoretical predictions on the basis of the expression (Eq. [37]) demonstrate reasonable agreement with the experimental data presented in Reference 15.
3. In a porous material with hollow pores of various size scale it is possible to achieve stronger reduction in the LTC than in the material with particle inclusions. Obviously, this is true for the model of the composite under consideration, in the absence of coherent precipitates.
4. The medium with pores of different size scales in the same host material is more preferable than a multilayer composite, different layers of which contain only pores of the same scale.

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REFERENCES

1. M.S. Dresselhaus, G. Chen, M.Y. Tang, R.G. Yang, H. Lee, D.Z. Wang, Z.F. Ren, J.P. Fleurial, and P. Gogna: *Adv. Mater.*, 2007, vol. 19, p. 1043.
2. J.F. Li, W.S. Liu, L.D. Zhao, and M. Zhou: *Nat. Asia Mater.*, 2010, vol. 2, p. 152.
3. H. Lee, D. Vashaee, D.Z. Wang, M.S. Dresselhaus, Z.F. Ren, and G. Chen: *J. Appl. Phys.*, 2010, vol. 107, p. 094308.
4. J.P. Heremans, C.M. Thrush, and D.T. Morelli: *Phys. Rev. B*, 2004, vol. 70, p. 115334.
5. R. Venkatasubramanian, E. Sivala, V. Colpitts, and B. O'Quinn: *Nature*, 2001, vol. 413, p. 597.
6. F. Hsu Kuei, S. Loo, F. Guo, W. Chen, S. Dyck Jeffrey, C. Uher, T. Hogan, E.K. Polychroniadis, and M.G. Kanatzidis: *Science*, 2004, vol. 303, p. 818.
7. T.C. Harman, P.J. Taylor, M.P. Walsh, and B.E. LaForge: *Science*, 2002, vol. 297, p. 2229.
8. T.M. Tritt and M.A. Subramanian: *MRS Bull.*, 2006, vol. 31, p. 188.
9. J.G. Snyder and E.S. Toberer: *Nat. Mater.*, 2008, vol. 7, p. 105.
10. L. Rayleigh: *Philos. Mag.*, 1892, vol. 34, p. 481.
11. J.C. Maxwell-Garnet: *Philos. Trans. R. Soc. Lond. A*, 1904, vol. 203, p. 385.
12. Ch. Zhou, S. Birner, Y. Tang, K. Heinselman, and M. Grayson: *Phys. Rev. Lett.*, 2013, vol. 110, p. 227701.
13. N. Neophytou, X. Zianni, H. Kosina, S. Frabboni, B. Lorenzi, and D. Narducci: *Nanotechnology*, 2013, vol. 24, p. 205402.

14. K. Biswas, J. He, Q. Zhang, C. Uher, V.P. Dravid, and M.G. Kanatzidis: *Nat. Chem.*, 2011, vol. 3, p. 160.
15. K. Biswas, J. He, I.D. Blum, C.I. Wu, T.P. Hogan, D.N. Seidman, V.P. Dravid, and M.G. Kanatzidis: *Nature*, 2012, vol. 489, p. 414.
16. R.H. Tarkhanyan and D.G. Niarchos: *Int. J. Therm. Sci.*, 2013, vol. 67, p. 107.
17. R.H. Tarkhanyan and D.G. Niarchos: *J. Mater. Res.*, 2013, vol. 28, p. 2316.
18. M. Kaviany: *Principles of Heat Transfer in Porous Media*, Springer, New York, 1991.
19. A. Majumdar: *ASME J. Heat Transf.*, 1993, vol. 115, p. 7.
20. R. Prasher: *J. Appl. Phys.*, 2006, vol. 100, p. 064302.
21. Z. Tian, J. Garg, K. Esfarjani, T. Shiga, J. Shiomi, and G. Chen: *Phys. Rev. B*, 2012, vol. 85, p. 184303.
22. J. He, S.N. Girard, M.G. Kanatzidis, and V.P. Dravid: *Adv. Funct. Mater.*, 2010, vol. 20, p. 764.
23. J. Callaway and H.C. Von Baeyer: *Phys. Rev.*, 1960, vol. 120, p. 1149.
24. M.V. Jambunathan: *Ann. Math. Stat.*, 1954, vol. 25, p. 401.
25. J.M. Ziman: *Electrons and Phonons*, Oxford University Press, Oxford, 1960.
26. C. Kittel: *Introduction to Solid State Physics*, Wiley, New York, 1971.
27. B. Qiu, H. Bao, G. Zhang, Y. Wu, and X. Ruan: *Comput. Mater. Sci.*, 2012, vol. 53, p. 278.