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High-temperature phonon thermal conductivity of nanostructures

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Phonon propagation in the disordered nanostructures at a high (about the Debye temperature or higher) temperature is considered. Scattering at the grain boundaries is assumed to be the main mechanism restricting the thermal conductivity. Influence of the structure (the grain size and its dispersion, the pore diameter and their volume concentration, and the intergrain interface structure) as well as temperature on the thermal conductivity is discussed.

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I. INTRODUCTION

The problem of short-wavelength phonon transport in granular materials becomes interesting due to its possible application for production of new coatings with minimal thermal conductivity (TC). Such coatings are used, e.g., for the thermal protection of gas turbines. This provides the main possibility to increase the service temperature of these turbines, because third generation of superalloys (which are the basic materials now) are approaching the practical upper limit of temperature.[1] The substrate temperature can be decreased by 100–300 K by using the thermal barrier coatings, allowing reduction in cooling air temperature and consequent increase of the engine efficiency. On the other hand, the use of the thermal barrier coatings allows to fill the temperature capability gap between superalloys and ceramic matrix composites,[1] the next generation materials with improved temperature capability, which still require further development.

It is apparent that the large number of the intergrain boundaries reduces the phonon mean free path; whereas, the short-wavelength phonon propagation is the most important mechanism of TC in dielectrics at high temperatures ($T \gtrsim T_D$, where T_D is the Debye temperature). Really, decrease of TC in nanocrystals has been predicted theoretically[2] and observed in the experiments.[2,3]

Klemens and Gell[2] used the lattice wave approach to consider different mechanisms that affect the phonon mean free path. They assumed the phonon-phonon interaction as the main mechanism that determined TC of the bulk materials and showed that TC can be essentially reduced due to wave scattering at the grain boundaries and impurities in the granular materials. It is apparent that the large number of the intergrain boundaries impedes understanding of the phonon transport in terms of the lattice wave theory. Indeed, Chen *et al.*[4] showed the importance of the structure of the granular material on the phonon transport. They demonstrate that the model where the phonons are considered as particles sometimes is more appropriate than the lattice wave model. It seems also that the commonly accepted continuum approximation is not appropriate when the intergrain transport of the phonons that wavelength is comparable with the lattice constant is considered.

In this paper we consider the phonon transport in the granular material assuming scattering at the grain boundaries as the main mechanism that determined TC. This means that correction to TC due to the grain boundaries prevails influence of the phonon-phonon scattering. Such a situation has been really observed in the experiments.[5–7] This is especially important for the applications where nanostructuring is used to reduce TC considerably.

We start with the phonon states that initially are localized at an individual grain and then consider the hopping transport of such the local phonons. This allows us to apply the Green's function technique, which is well developed for the disordered materials, to consider the thermal conductivity. The expression obtained for TC makes it possible for us to estimate the influence of different factors: the grain size, its dispersion, porosity (the pores diameter as well as their volume concentration), structure of the intergrain boundary, and temperature on the TC value.

The paper is organized as follows. In the Sec. II we study the simplest one-dimensional models; this is necessary for the justification of our assumptions. It is shown that the short-wavelength phonons are really localized at the grains, whereas their hopping between neighboring grains can be considered as perturbation. Dependence of the hopping parameter on the distance between the grains is estimated. This dependence is shown to be powerlike, but not exponential as it happens for the electron hopping. This makes inappropriate the percolation models commonly used to consider the electron transport.

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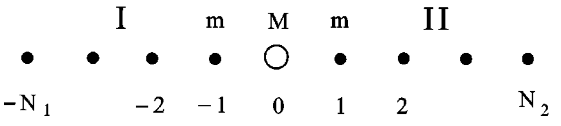

FIG. 1. The one-atom contact of two 1D chains.

In the Sec. III we propose the model of the hopping phonon transport and use it to consider TC. In Sec. IV we study the dependence of TC of the granular materials on the mean grain size, the distance between the grains, as well as the mean square of deviation of these variables from their mean values.

The units where the Planck constant $\hbar$ and the Boltzmann constant k_B are equal to unity are adopted. We include these constants only in Eqs. (20) and (22) to facilitate their usage in calculations.

II. PHONONS AT A BOUNDARY: TWO SIMPLEST MODELS

A. Impurity atom in a 1D chain

Let us consider a contact of two one-dimensional (1D) chains of atoms of the same mass m connected by springs of equal elasticity α (Fig. 1). The numbers of atoms in the chains are N_1 and N_2, respectively. Subscript n indicates each atom, so that $n=0$ for the boundary atom that distinguishes from others only by its mass M. Displacements of atoms u_n obey the motion equations:

$$m\ddot{u}_n=-\alpha(2u_n-u_{n+1}-u_{n-1}), \quad n\neq 0,$$

$$M\ddot{u}_0=-\alpha(2u_0-u_1-u_{-1}), \quad n=0. \tag{1}$$

To find the solution of Eq. (1) we fix the ends of the chains $u_{-N_1}=u_{N_2}=0$ and assume $u_n(t)=e^{-i\omega t}u_n^{I,II}$, where ω is the phonon frequency, and $u_n^{I,II}$ are displacements of atoms at each (I or II) chain, so that

$$u_n^I=U_q^I e^{iqn}+U_{-q}^I e^{-iqn}, \quad n<0,$$

$$u_n^{II}=U_q^{II} e^{iqn}+U_{-q}^{II} e^{-iqn}, \quad n>0. \tag{2}$$

Substitution of these equations into Eq. (1) yields

$$\omega=2\sqrt{\frac{\alpha}{m}}\sin\frac{q}{2}. \tag{3}$$

Such a dependence of frequency ω on the wave vector q is typical for the acoustic phonons. For the Debye frequency in our model we have $\omega_D=2\sqrt{\alpha/m}$. In addition, the substitution (2) leads to the system of uniform equations for U_q^I, U_{-q}^I, U_q^{II}, and U_{-q}^{II}. In order for this system to have a nontrivial solution, the following equation should be satisfied:

$$\omega^2(M-m)(1-e^{2iqN_1})(1-e^{2iqN_2})$$
$$+2i\alpha\sin q[1-e^{2iq(N_1+N_2)}]=0. \tag{4}$$

Equations (3) and (4) determine the phonon spectrum of the chains. There are two limits that are interesting to consider.

(a) The long-wavelength phonons. For these phonons $q\ll\pi$, therefore $\sin q\sim q$ and $\omega^2\sim q^2$. This allows to omit the first term in Eq. (4). Then we obtain

$$1-e^{2iq(N_1+N_2)}=0.$$

The same equation arises also if we assume $M=m$. This is a familiar condition for quantization of the standing wave in the box, whose width is N_1+N_2. The first term in Eq. (4), if taken into account, leads to the scattering of this wave at the impurity $n=0$.

(b) The short-wavelength phonons. For these phonons $q\simeq\pi$. Then $\sin q\sim(\pi-q)\ll 1$, $\omega^2\sim 4\alpha/m=\omega_D^2$, i.e., the second term in Eq. (4) is small in comparison with the first one. Omitting the second term, we find

$$1-e^{2iqN_1}=0 \text{ or } 1-e^{2iqN_2}=0.$$

This means that the short-wavelength phonons are localized either in the left or right chains. Influence of the second term can be considered as hopping of these localized phonons between the chains. To determine the correction to the phonon energy, arising due to this hopping, we assume $q=\pi-p$, where $p=\pi n/N_1+\delta p$ and $\delta p N_1\ll 1$. Then

$$\delta p=\frac{\alpha p}{\omega^2 N_1(m-M)}$$

and

$$\delta\omega=-\frac{1}{4}\left(\frac{\pi n}{N_1}\right)^2\frac{\alpha}{N_1\omega^2(m-M)}\sqrt{\frac{\alpha}{m}}. \tag{5}$$

It is easy to understand the difference between the cases (a) and (b). Indeed, the atoms in the case (a) move in the same direction, and the distance between them changes slowly. The effect of impurity at $n=0$ could be essential only if its mass is comparable with the mass of all the atoms in that part of the chain whose size is about the wavelength. Otherwise, the small parameter of the order of $|M-m|/(N_1+N_2)$ arises.

On the contrary, the atoms in the case (b) move in the opposite direction. Short-wavelength phonons in this case represent oscillation of the two-atom "molecule" propagated along the chain due to resonance between all such molecules. Frequency of this oscillation depends on masses of the atoms. This makes the molecule at the boundary to be out of the resonance, and so impedes the short-wavelength phonons to cross the boundary.

B. Many-atomic interface between two 1D chains

Consider now an interface of $2N_0$ atoms presented in Fig. 2. We suppose $N_0\gg 1$; the mass of the chains atoms is m, and that of the interface atoms is M.

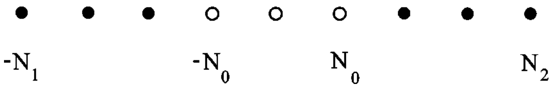

FIG. 2. The $2N_0$-atom contact of two 1D chains.

The motion equations are

$$m\ddot{u}_n = -\alpha(2u_n - u_{n+1} - u_{n-1}), \quad |n| > N_0,$$

$$M\ddot{u}_0 = -\alpha(2u_n - u_{n+1} - u_{n-1}), \quad |n| \leqslant N_0. \tag{6}$$

We assume $u_n(t) = e^{-i\omega t} u_n^{I,II,\,int}$, where $u_n^{I,II,\,int}$ are the displacements of atoms at each (I or II) chain and the interface (int):

$$u_n^{I} = U_q^{I} e^{iqn} + U_{-q}^{I} e^{-iqn}, \quad n < -N_0,$$

$$u_n^{int} = U_Q e^{iQn} + U_{-Q} e^{-iQn}, \quad |n| \leqslant N_0,$$

$$u_n^{II} = U_q^{II} e^{iqn} + U_{-q}^{II} e^{-iqn}, \quad n > N_0. \tag{7}$$

The relation between the frequency ω and the wave vectors q and Q that follows after substitution of these equations into Eq. (6) is

$$\omega^2 = \frac{2\alpha}{m}(1 - \cos q) = \frac{2\alpha}{M}(1 - \cos Q). \tag{8}$$

The wave vector of the phonons in the chains q should be real, however, the wave vector of the phonons in the interface Q can be either real or complex. The latter is possible for the phonons whose energies prevail the Debye energy at the interface Ω_D, if $\Omega_D > \omega_D$ (Fig. 3). Complex value of Q means attenuation of the phonon in the interface region. This impedes the phonon transport. We shall consider only the phonons with $q \leqslant q_{max}$, whose energies are less than Ω_D.

Assuming the interface to be thin $[1 \ll N_0 \ll (2|p|)^{-1}$, where $p = \pi - q \ll 1]$, we can extend the amplitudes $u_n^{I,II}$ into the interface region $|n| \leqslant N_0$ and write the boundary condition for them and their derivatives $\partial_n u_n^{I,II}(0) = \partial u_n^{I,II}/\partial n = -ip(U_q^{I,II} - U_{-q}^{I,II})$ at the interface $n = 0$.

$$\begin{pmatrix} u_n^{II}(0) \\ \partial_n u_n^{II}(0) \end{pmatrix} = \hat{T} \begin{pmatrix} u_n^{I}(0) \\ \partial_n u_n^{I}(0) \end{pmatrix}, \tag{9}$$

where $\hat{T} = \|t_{ij}\|$ is the 2×2 matrix of the real values. After some algebra (see the Appendix), we obtain, for its matrix elements in our model

$$t_{11} = t_{22} = \frac{2\cos Q/2}{\sin Q}\{(1+N_0)\sin(1+4N_0)Q/2 + N_0 \sin(3+4N_0)Q/2\},$$

$$t_{12} = -\frac{1}{\sin Q}\{(1+N_0)^2 \sin 2N_0 Q + N_0^2 \sin 2Q(1+N_0) + 2N_0(1+N_0)\sin Q(1+2N_0)\},$$

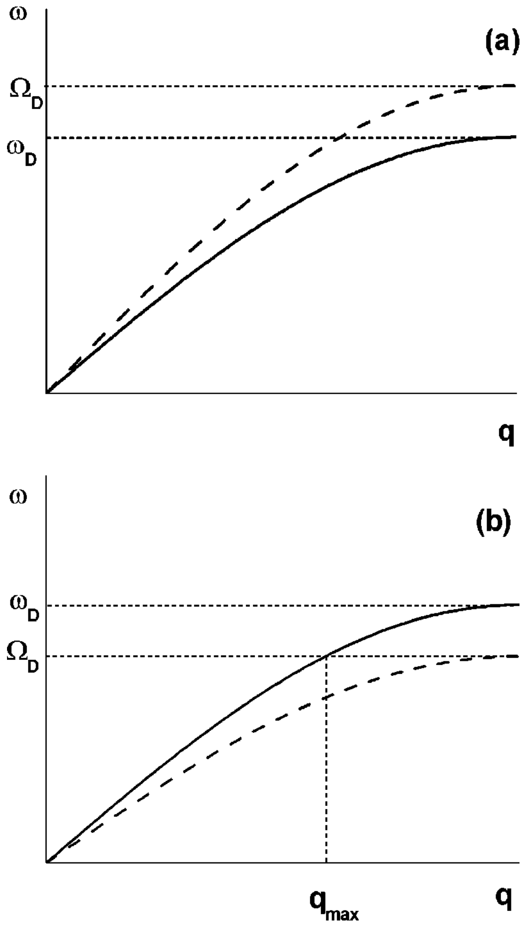

FIG. 3. Dependences of frequency on the wave vector for the phonons in the chains (solid line) and the interface (dashed line).

$$t_{21} = -\frac{2\cos Q/2}{\sin Q}\{\sin(1+4N_0)Q/2 + \sin(3+4N_0)Q/2\}.$$

Boundary conditions, Eq. (9), together with the conditions at the ends of the chains $u_{-N_1} = u_{N_2} = 0$ lead to the system of four uniform equations for U_q^I, U_{-q}^I, U_q^{II}, and U_{-q}^{II}. This system has nontrivial solutions only if

$$(1 - e^{2ipN_2})(1 - e^{2ipN_1}) - 2ip\frac{t_{11}}{t_{21}}[1 - e^{2ip(N_1+N_2)}] = 0, \tag{10}$$

where

$$-\frac{t_{11}}{t_{21}} = N_0 + \frac{\sin[(1+4N_0)Q/2]}{\sin[(1+4N_0)Q/2] + \sin[(3+4N_0)Q/2]}.$$

Correction to the phonon energy due to the interchain hopping [similar to that of Eq. (5)] is

$$\delta\omega = \frac{1}{8}\left(\frac{\pi n}{N_1}\right)^2 \frac{t_{11}}{N_1 t_{21}} \omega_D. \tag{11}$$

III. PHONON TRANSPORT IN THE GRANULAR MATERIAL: TRANSFER HAMILTONIAN APPROACH

Analysis of the simple models shows that a boundary impedes short-wavelength phonon transport across it. This makes difficult to consider the phonon transport as a wave propagation, if the number of boundaries is large. This is the case of the granular materials. To avoid this difficulty, we start with phonons or oscillating modes initially localized in each individual grain. The number of these modes is equal to $3N_i$, where N_i is the number of atoms in the ith grain. Frequencies of these modes are individual to each grain too. We assume, however, that the grains are large, so that the frequencies are distributed homogeneously over the interval $[0,\omega_D]$. Transport of these modes occurs due to their hopping between the neighboring grains; this can be considered as a perturbation. We write the transfer Hamiltonian as follows:

$$H=\sum_{i,k}\omega_{ik}\left(a^{+}_{ik}a_{ik}+\frac{1}{2}\right)+\sum_{i,k,j,p}(t_{ijkp}a^{+}_{ik}a_{jp}+\text{H.c.}),\tag{12}$$

where the Bose operators a^{+}_{ik} (a_{ik}) create (annihilate) the $k\equiv k_i$th localized phonon mode at the ith grain. The first term in Eq. (12) corresponds to the phonon energies of the individual modes and the second one to the hopping between them.

To estimate the value of the hopping integral t_{ijkp}, let as return to the simple models of two chains considered in the Sec. II. Then the Hamiltonian (12) can be rewritten as

$$H=\sum_{k}\omega_k\left(a^{+}_{k}a_{k}+\frac{1}{2}\right)+\sum_{p}\omega_p\left(b^{+}_{p}b_{p}+\frac{1}{2}\right)+\sum_{k,p}(t_{kp}a^{+}_{k}b_{p}+\text{H.c.}),$$

where the Bose operators a_k and b_p correspond to the phonons at the chains I and II, k and p are the wave vectors of these phonons, measured from the band edge, i.e., $\omega_k=\omega_D\cos k/2$ and $\omega_p=\omega_D\cos p/2$. The Schrödinger equation $H\Psi=E\Psi$ following from this Hamiltonian leads to the equation for the energy spectrum E,

$$1+\sum_{k,p}\frac{t^2_{kp}}{(\omega_k-E)(\omega_p-E)}=0.\tag{13}$$

For $t_{kp}=0$, the energy spectrum is determines by the zeros of the denominator, Eq. (13), i.e., $E=\omega_k$ and $E=\omega_p$. For small t_{kp} we write $E=\omega+\delta\omega$, where ω is one of the zeros of the denominator, Eq. (13), and $\delta\omega$ is the correction. This correction is equal to Eq. (5), if

$$t^2_{kp}=\frac{\alpha\left(1-\cos\frac{p}{2}\right)\left(1-\cos\frac{k}{2}\right)}{N_1N_2(m-M)}=\frac{\alpha(\omega_D-\omega_k)(\omega_D-\omega_p)}{N_1N_2(m-M)\omega_D^2},$$

or Eq. (11), if

$$t^2_{kp}=-\frac{t_{11}}{t_{21}}\frac{\omega_D^2}{N_1N_2}\left(1-\cos\frac{p}{2}\right)\left(1-\cos\frac{k}{2}\right)=-\frac{t_{11}}{t_{21}}\frac{(\omega_D-\omega_k)(\omega_D-\omega_p)}{N_1N_2}.$$

We shall use this estimation further.

Using the Hamiltonian (12), it is possible to determine the total phonon current to the ith grain from all neighboring grains.

$$Q_i=i\sum_{j,k,p}\omega_{ik}\langle(t_{ijkp}a^{+}_{ik}a_{jp}-\text{H.c.})\rangle.$$

Here the brackets $\langle\ \rangle$ denote the thermodynamic average. In the second order of the perturbation theory with respect to t_{ijkp}, this value is equal to

$$Q_i=\sum_{j,k,p}\omega_{ik}|t_{ijkp}|^2(n_i-n_j)\,\delta(\omega_{ik}-\omega_{jp}),\tag{14}$$

where T_i is the temperature of the ith grain, the Bose function $n_i=[e^{\omega_{ik}/T_i}-1]^{-1}$ is the number of phonons with the energy ω_{ik} at the ith grain. In particular, $n_i=T_i/\omega_{ik}$ under the high temperatures $T_i\gg\omega_{ik}$, so that

$$Q_i=\sum_{j,k,p}|t_{ijkp}|^2(T_i-T_j)\,\delta(\omega_{ik}-\omega_{jp}),$$

and TC becomes temperature independent.

The δ function in Eq. (14) means conservation of the phonon energy under hopping. There are two limits that are interesting to consider. First, the mean spacing between the phonon levels ω_{ik} significantly exceeds the hopping integral $|t_{ijkp}|$. This is possible for the small grains or the phonons whose energies are close to the band edge ω_D. Such phonons are localized and do not participate in the thermal transport. Indeed, the phonon with certain energy $\hbar\omega_p$ cannot move to the neighboring grain, if the level with the same energy is absent there. This is the Anderson localization of the phonons, which also restricts TC. Let us consider the contact of two one-dimensional chains studied in Sec. II. In the first approximation the phonon states of the chains are localized, and if $N_1\neq N_2$, their energies are different. Corrections to these energies due to the hopping are determined by Eq. (5),

$$\delta\omega\sim-\frac{p^2t\omega_D}{4N_{1,2}},$$

where

$$t=\frac{\alpha}{(M-m)\omega_D^2}=\frac{m}{4(M-m)}.$$

The wave vector p is measured from the band edge; it is small for the Debye phonons with $\omega_p\approx\omega_D$. Spacing between the levels of the different chains is of the order of

$$\Delta\omega \sim \frac{\omega_D}{2}\cos\frac{q}{2}\Delta q,$$

i.e.,

$$\left|\frac{\delta\omega}{\Delta\omega}\right| \sim \frac{p^2 t}{2\pi\cos\dfrac{q}{2}} \sim \frac{pt}{2\pi}.$$

This means that for $t \sim 1$, $\delta\omega \ll \Delta\omega$, and all the phonon states are localized.

This is, however, characteristic of the 1D chain. For the 3D case we have

$$\delta\omega \sim -\frac{p^2 t\omega_D}{4N_z},$$

meanwhile

$$\Delta\omega \sim \frac{\omega_D}{N_j},$$

i.e.,

$$\left|\frac{\delta\omega}{\Delta\omega}\right| \sim \frac{pt}{2\pi}N_x N_y = \frac{pt\overline{S}}{2\pi a^2}.$$

The phonons are localized if this value is less than $4/x_c$, where $x_c \approx 0.35$ is a percolation threshold for the 3D site problem (see Ref. 8 for the details). Thus, only the phonons with $p > p_c$, where $p_c \approx 8\pi a^2/(t\overline{S}x_c)$ is the mobility threshold, are delocalized and participate in the heat transport. To estimate correction to the TC, we have to replace $\omega_D \rightarrow \omega_D\cos(p_c/2)$.

The value of p_c is small if $\overline{S} = d^2$; however, it increases for the smaller values of $\overline{S}$. This could be a result of porosity. Indeed, for the point contact of the two spheres (the porosity is about $1-\pi/6 \approx 1/2$), $N_x N_y = 1$, and we return back to the 1D case where all phonon states are localized.

Consider now the second limit. Suppose the mean spacing between the phonon levels ω_{ik} is considerably less than the hopping integral $|t_{ijkp}|$. This is characteristic of large grains and the phonons that energies are far off the mobility edge. Assuming the phonon energies to be continuously distributed on the interval $[0,\omega_D]$, we change the summation over the states of the jth grain in Eq. (14), with the δ function for its multiplication by the 1D density of the states $3N_{jz}/(2\omega_D)$ [$N_{jz} = d/a$ is the number of atoms of the jth grain in one (z) direction]. Indeed, each oscillating mode of the ith grain connects with each mode of the jth grain via the hopping integral t_{ijkp}. However, this connection occurs at the boundary where each atom of the ith grain connects only with one atom of the jth grain. For this clear reason, $N_{jz} = N_j/(N_{jx}N_{jy})$, but not N_j itself arises in the density of states. This becomes more apparent if we consider the plane interface, where $t_{ijkp} \propto \delta(k_\parallel - p_\parallel)$ ($k_\parallel$ and $p_\parallel$ are the parallel to the grain boundary components of the wave vectors). This means that density of the phonon states with regards to one vector is one dimensional. Replacing also the summing over the states of the ith grain for the integration with the 3D density of states $3\omega_k^2 N_j/\omega_D^3$ and assuming $T_i \approx T_j$, from Eq. (14), we find

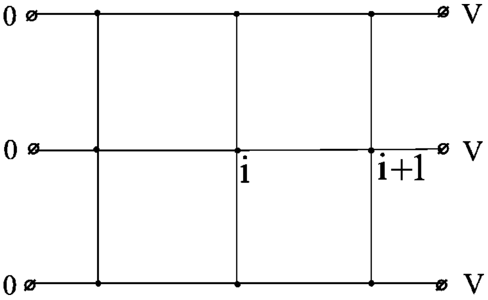

FIG. 4. The net of random resistors. For simplicity, only its 2D projection is presented.

$$Q_i = \frac{9}{2}\left(-\frac{t_{11}}{t_{21}}\right)(T_i - T_j)\frac{N_j N_{iz}}{\omega_D^4 N_{iz} N_{jz}} \times \int_0^{\omega_D} \frac{\left(\dfrac{\omega_k}{T}\right)^2 e^{\omega_k/T}}{(e^{\omega_k/T}-1)^2}(\omega_D - \omega_k)^2 \omega_k^2\, d\omega_k$$

or

$$Q_i = \left(-\frac{t_{11}}{t_{21}}\right)\omega_D \beta(T)\frac{S_{ij}(T_i - T_j)}{a^2}, \tag{15}$$

where

$$\beta(T) = \frac{9}{2}\theta^5 \int_0^{1/\theta} \frac{x^4 e^x}{(e^x-1)^2}\left(x - \frac{1}{\theta}\right)^2 dx$$

and

$$\theta = \frac{T}{T_D}.$$

Here S_{ij} is the area of the contact between the ith and jth grains, so that $(-t_{11}/t_{21})S_{ij}$ is a random function of i and j.

To determine the thermal conductivity, we have to add the values of Q_i over the grains in the unit layer. It is natural to interpret Q_i as an electrical current to the site i from its neighbors j, and the temperatures T_i and T_j as the potentials of these sites. In other words, we have to estimate the conductivity of the net of the random resistances whose values are $[\beta\omega_D(-t_{11}/t_{21})S_{ij}/a^2])^{-1}$. It is important that these random values do not have an exponential, but a powerlike dispersion.

IV. CONDUCTIVITY OF THE 3D CUBIC LATTICE OF THE RANDOM RESISTORS

We find the conductivity of the net presented in Fig. 4.

Let V_{ijk} be the potential of the site, the coordinates of which are i, j, k ($V_{0jk} = 0, V_{Njk} = V$), and $r_{i+1/2jk}$ is resistance of the cube edge between the sites i, j, k and $i+1,j,k$. The first Kirchhoff's law being written for the ith site is

$$\frac{V_{i+1jk}-V_{ijk}}{r_{i+1/2jk}}-\frac{V_{ijk}-V_{i-1jk}}{r_{i-1/2jk}}+\frac{V_{ij+1k}-V_{ijk}}{r_{ij-1/2k}}-\frac{V_{ijk}-V_{ij-1k}}{r_{ij-1/2\,k}}+\frac{V_{ijk+1}-V_{ijk}}{r_{ijk+1/2}}-\frac{V_{ijk}-V_{ijk-1}}{r_{ij\,k-1/2}}=0. \tag{16}$$

The current across the net is

$$I=\sum_{j,k}\frac{V_{i+1jk}-V_{ijk}}{r_{i+1/2jk}}. \tag{17}$$

Equation (16) can be solved numerically for any distribution of the resistance $r_{i+1/2jk}$. This can also be done analytically if we assume the small deviation of these values and the large number of neighboring sites.

Really, the solution of Eq. (16) for equal resistors ($r_{ijk}=r_0$) is $V_{ijk}=iV/N$, where N is the number of resistors in the direction of the bias application (z). Then $I=N_xN_yV/Nr_0$, where N_x and N_y are the number of resistors on the contact plane.

Let

$$\frac{1}{r_{i+1/2jk}}=\frac{1}{r_0}(1+\xi_{i+1/2jk}),\qquad V_{ijk}=\frac{V}{N}(i+\eta_{ijk}),$$

where $\xi_{i+1/2jk}$ and η_{ijk} are random variables with the zero mean. Suppose independence of the fluctuations of ξ at the different sites, and the mean square of these fluctuations at the same site to be σ^2, i.e., $\overline{\xi_{i+1/2jk}\xi_{i'+1/2j'k'}}=\sigma^2\delta_{ii'}\delta_{jj'}\delta_{kk'}$. Then the current across the net is

$$I=\frac{N_xN_yV}{Nr_0}+\delta I,$$

$$\delta I=\frac{V}{Nr_0}\sum_{j,k}\overline{(\eta_{i+1jk}-\eta_{ijk})\xi_{i+1/2jk}}$$

$$=\frac{V}{Nr_0}\sum_{j,k}\overline{\eta_{ijk}(\xi_{i-1/2jk}-\xi_{i+1/2jk})}. \tag{18}$$

We assume homogeneity of the fluctuations, i.e., their independence of the particular site. This means that all averages under sums in Eq. (18) are invariant under the shift of all indices on the same vector, i.e., $i\rightarrow i+a$, $j\rightarrow j+b$, and $k\rightarrow k+c$.

To evaluate the averages for the current expression (18), it is necessary to rewrite Eqs. (16) in terms of ξ and η, then multiply them by the correspondent ξ and average. This routine leads to the infinite system of the linked equations for the averages $\overline{\eta\xi}$ that connect the fluctuations of the conductances ξ and the potentials η at the different sites of the net. To unlink the equations, we assume the number of neighbors for each site in the net n to be large. Then it is possible to consider only the averages connected to the nearest neighbors. Assuming also the fluctuations to be small ($|\xi|\ll 1, |\eta|\ll 1$), we write

$$\overline{\eta_{i+1jk}\,\xi_{i+1/2\,jk}}-n\,\overline{\eta_{ijk}\,\xi_{i+1/2\,jk}}+4\gamma+\sigma^2=0,$$

$$\overline{\eta_{i-1jk}\,\xi_{i-1/2\,jk}}-n\,\overline{\eta_{ijk}\,\xi_{i-1/2\,jk}}+4\delta-\sigma^2=0,$$

where $\gamma\sim\overline{\eta_{i\,j+1\,k}\xi_{i+1/2jk}}$ and $\delta\sim\overline{\eta_{i\,j-1\,k}\xi_{i-1/2jk}}$ are the averages connected the next neighboring sites. Omitting them, we obtain

$$\overline{\eta_{i+1jk}\,\xi_{i+1/2\,jk}}=-\frac{\sigma^2}{1+n},\qquad \overline{\eta_{i-1jk}\,\xi_{i-1/2\,jk}}=\frac{\sigma^2}{1+n},$$

so that

$$\delta I=-\frac{2VN_xN_y}{Nr_0}\frac{\sigma^2}{1+n},$$

and

$$r=r_0\left(1+\frac{2\sigma^2}{1+n}\right). \tag{19}$$

It can be shown that $|\gamma|\sim|\delta|\sim\sigma^2/[n(1+n)]$; they are smaller than $n\gg 1$.

The value of mean conductivity is $r_0^{-1}=\beta\omega_D t\overline{S}/a^2$, where $\overline{S}$ is the mean area of the intergrain boundary and $t=\langle|t_{11}/t_{21}|\rangle$ depends only on the boundary structure. Then we can write TC as follows:

$$\kappa_{ph}=\frac{1}{k_B\,a^2d}\beta(T)t\overline{S}\omega_D\Phi(\sigma). \tag{20}$$

Here $\Phi(\sigma)$ is the factor relevant to the disorder. Equation (20) yields for it

$$\Phi=\left(1+\frac{2\sigma^2}{n}\right)^{-1}. \tag{21}$$

We solved numerically the system (16) for the cube with 100×100×100 sites by iterative Lanczos (or conjugate gradient) algorithm outlined in Ref. 9. Accuracy of the solution has been estimated by overall current deviation that equals to sum of the absolute values of current imbalance in each site. The resulting deviation in our calculations typically was about 10^{-13} of the value of total current. This value characterizes very high accuracy of solution as well as accuracy of determining total current through cube. However, due to the finite size of the cube, there is dispersion of the current for the different realization of the random values r_{ijk}^{-1}. Figure 5 presents the average value of factor Φ obtained from numerical solution of Eq. (16) for different random realizations of r_{ijk}^{-1} together with the factor Φ following from Eq. (21). Conductivities r_{ijk}^{-1} were assumed to be distributed homogeneously on the interval $[1-\delta/2,\,1+\delta/2]$ (in calculations they were produced by noise number generator), this yields $\sigma^2=\delta^2/12$.

Analysis of dispersion of the Φ factor for the maximal fluctuations of conductivity, i.e. for $\delta=2$, yields the following average values of Φ and its standard deviation: 0.8745 ± 0.0003. The calculations performed for the 30×30×30 and 50×50×50 cube dimensions yield the following results for Φ: 0.8723 ± 0.0011 and 0.8743 ± 0.0021, respectively. This statistics was derived from results for the six random

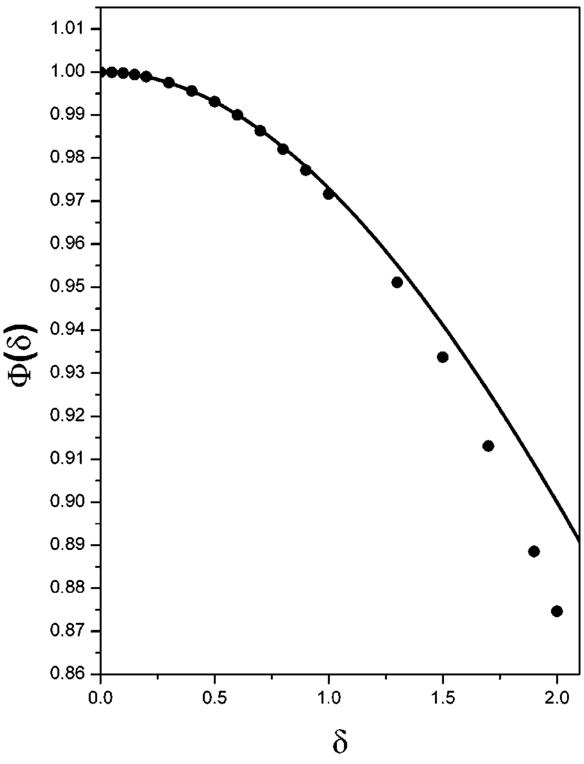

FIG. 5. Factor of disorder. The bold line corresponds to Eq. (21), dots represent average value of Φ (over six random realizations of the conductivities) obtained from numerical solution of Eq. (16).

realizations of the conductivities. Standard deviation generally decreases with increasing cube size, whereas the current value changes slightly. This gives assurance that the results for $100\times100\times100$ cube reproduce the thermodynamic limit for the current with the accuracy being equal to the standard deviation of Φ for various random realizations of r_{ijk}^{-1} (for $\delta=2$ it is equal to 0.0003). Obviously, the relative value of the standard deviation should decrease with decreasing δ. All the above, together with Fig. 5, make apparent that Eq. (21) can be used for the qualitative estimations even for the large fluctuation of the conductivities. It seems that this is always the case if $n\gg1$; this makes the influence of the grain size fluctuations not so essential.

V. DISCUSSION

In this paper we propose the model to describe the high-temperature thermal conductivity of the nonmetalic nanostructures. We show that the short-wavelength phonons, which are of main importance for the high-temperature thermal conductivity, are strongly localized at the grains. Such phonon confinement has been investigated numerically for the superlattices;[10] the considerable decrease of TC due to change of the phonon spectrum caused by the boundaries has been found. The jump of the temperature at the grain boundary caused by the phonon confinement can be considered as a possible mechanism of the Kapitza resistance,[11] this allows one to use numerical methods[12–14] to estimate TC of the structure. Nevetheless, the analytical expression (20) we obtained allows us to estimate qualitatively the influence of different factors on the TC of nanostructures.

The value of TC is determined as a function of two parameters t and σ. First of them corresponds to the transparency of the intergrain boundary for the short-wavelength phonons. The second one corresponds to the disorder that is due to deviation of the grain sizes, the area of the intergrain boundary, and its width. Both the parameters depend on many factors and should be considered as phenomenological. Nevertheless, it would be interesting to estimate the influence of different factors on their values.

For the t parameter at a one-atom 1D interface, we obtain $t\propto(M-m)^{-1}$, so that it becomes large if $M\approx m$. This should be the case if velocities of the sound and the Debye frequencies of the grain material and the interface are close. In particular, for the interface of the crystalline and amorphous $\mathrm{Al_2O_3}$, this value is $S/|S_{\mathrm{crystalline}}-S_{\mathrm{amorphous}}|\approx21.2$. To reduce it, some impurities that change the interface density or elasticity should be introduced.

To estimate the influence of the interface width, we can use Eq. (10). If the Debye frequencies of the grain material and the interface are close, then $Q\rightarrow\pi$. If also $(\pi-Q)N_0 \ll1$, then t becomes close to its value for the one-atom interface. Otherwise, we have an oscillating dependence of t on the interface width. In the 3D case, this means an increase of the σ value, which leads to a decrease of the TC.

The grain-size dependence of TC is not simple. Two values: the grain size d and the mean area of the interface $\bar{S}$ affect it, and the relation $\bar{S}\propto d^2$ is not always satisfied. Equation (20) determines TC of the large grains. For the smaller grains the localization of the short-wavelength phonons becomes appreciable. To take this into account, we have to substitute $\omega_D\rightarrow\omega_D\cos p_c/2$ in this expression. Here $p_c \approx8\pi a^2/(t\bar{S}x_c)$ is the mobility threshold, $x_c\approx0.35$ or $x_c \approx0.6$ for the three- or two-dimensional structures, respectively.[8] The value of p_c becomes comparable with $\pi/2$ (all the short-wavelength phonons are localized) when $\bar{S} \approx16a^2/(tx_c)$. For $t\sim1$, this means that the size of the interface region is comparable with six lattice constants. This is possible even for the large ($d\gg6a$) grains due to porosity. This may be the possible explanation of the experiments of Ref. 7, where a sharp jump of TC at $d=10$ nm in yttria-stabilized zirconia ($a\approx0.5$ nm) nanostructured thin films has been observed. TC of the nanostructure of smaller grains is due to the large-wavelength phonons ($\lambda_{ph}\gg d$) that are not localized. The number of such phonons is $N_{ph}\sim d^{-3}$; thus, it is possible to expect an increase $\kappa\sim d^{-2}$ of TC for the very small grain-size structures.

The temperature dependence of TC is determined by the β factor (Fig. 6). It is independent of the grain size. At small temperatures ($T\lesssim T_D$), it increases due to increase of the number of the phonons responsible for the heat transport. At high temperatures ($T\gg T_D$) it is constant. Such a behavior of TC follows also from the commonly used expression $\kappa =1/3C_VVd$, where the heat capacity C_V is a well-known function of temperature and V is the velocity of sound. It should be noted, however, that the high-temperature value of TC we obtain is about of one order less than what the

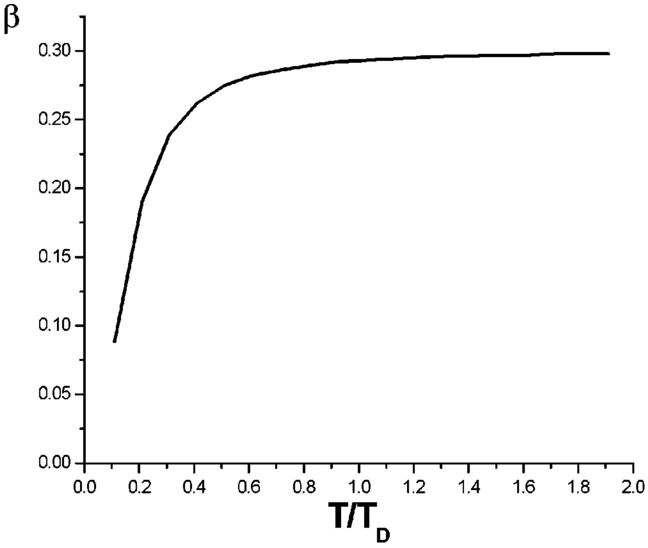

FIG. 6. Temperature factor.

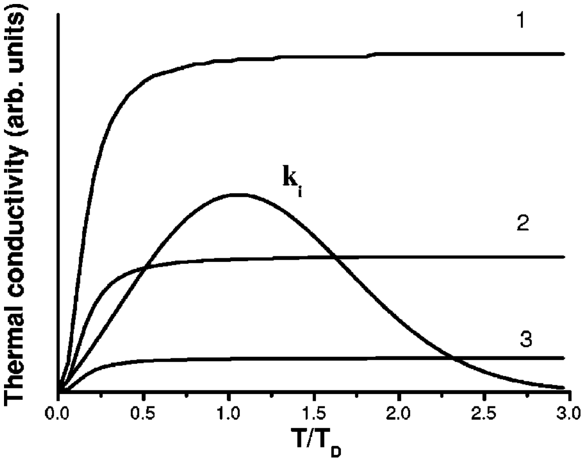

FIG. 7. Temperature dependence of the bulk κ_i and a boundary κ_{ph} parts of TC for the different grain-size nanostructures ($d_1 > d_2 > d_3$).

commonly used expression yields; i.e., mean free path l_{ph} is less than the grain size. This is due to the confinement of the high-energy phonons at the grains.

The decrease of TC, which is observed in some experiments, is due to the phonon-phonon interaction that has not been taken into account. To consider it in the framework of our model, let us assume that some resistors are series connected to r_{ijk} (Fig. 4). Such an assumption valids if the phonon scattering at the grain boundaries and due to the phonon-phonon interaction can be considered independently, so that $1/l = 1/l_B + 1/l_{ph}$. This concerns also any other bulk mechanism of the phonon scattering. The value of this resistance is $r_i = (\kappa_i d)^{-1}$, where κ_i is the bulk part of TC. For the phonon-phonon interaction it can be estimated as $\kappa_i = 1/3 C_V V l_{ph}$, where $l_{ph} = (20 T_m a)/(\gamma^2 T)$ is the phonon mean free path, T_m is the melting point, and γ is the Gruneisen constant. Then $R = r_i + r_{ijk}$, $r_{ijk} \approx a^2/[\beta(T)\omega_D t d^2]$, and for the effective value of TC, $\kappa = 1/(Rd)$, we obtain

$$\kappa = k_B T \int_0^{1/\theta} \frac{\kappa_i B(x) t \overline{S} \Phi}{\hbar k_B^{-1} \kappa_i a^2 d + k_B T_D B(x) t \overline{S} \Phi} dx,$$

where

$$B(x) = \frac{9}{2} \theta^4 \frac{x^4 e^x}{(e^x - 1)^2} \left(x - \frac{1}{\theta} \right)^2, \quad \theta = \frac{T}{T_D}. \tag{22}$$

This expression can be simplified if we substitute x by its average value $\overline{x}$,

$$\kappa = \frac{\kappa_i \beta \tilde{t} \overline{S} \omega_D \Phi}{k_B^{-1} \kappa_i a^2 d + \beta \tilde{t} \overline{S} \omega_D \Phi},$$

however, in this case the trial parameter $\tilde{t} = B(\overline{x}) t/\beta$ becomes dependent on the temperature.

It is apparent that the total TC is determined by the minima value of κ_{ph} and κ_i. Temperature dependences of both the values for the different grain sizes are presented in Fig. 7. For a large grain-size nanostructure (curve 1) $\kappa_i \ll \kappa_{ph}$, i.e., $\kappa \approx \kappa_i$. Decreasing of the grain size results in some temperature interval where $\kappa_i > \kappa_{ph}$ (curve 2), i.e., $\kappa \approx \kappa_{ph}$ and the nanostructuring is important. This temperature interval increases for a smaller grain size (curve 3).

It should be noted that temperature dependence of TC allows one to estimate what mechanism prevails in a certain experiment: phonon-phonon interaction or scattering at the grain boundaries. For the first case TC decreases as $\kappa \propto 1/T$, whereas for the latter one, κ increases or becomes constant. Such a behavior of TC has been also obtained in Ref. 2.

It seems possible that change of the phonon spectrum due to confinement could change also the phonon-phonon part of the TC, like it occurs in the superlattices.[10] This is the subject of futher investigations.

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APPENDIX

To obtain the boundary conditions (9) that connect the amplitudes $u_n^{I,II}$ at the interface, we have to relate the values U_q^I, U_{-q}^I, U_q^{II}, U_{-q}^{II}, U_Q, and U_{-Q}. To do this, the motion equations (6) should be written for the bordered atoms $n = \pm(N_0+1)$ and $n = \pm N_0$. In particular, for the atom at $n = -N_0 - 1$, we have

$$m\omega^2 u^I_{-N_0-1} = \alpha(2u^I_{-N_0-1} - u^{int}_{-N_0} - u^I_{-N_0-2} - u^I_{-N_0} + u^I_{-N_0}). \tag{A1}$$

Here $u^I_{-N_0}$ is the solution of the first equation of Eq. (6) expanded into the site $n=-N_0$. Note that the amplitude $u^I_{-N_0}$ obeys the first equation of Eq. (6), whereas $u^{int}_{-N_0}$ the second one. Then Eq. (A1) reduces to

$$u^I_{-N_0}=u_{-N_0},$$

$$u_{-N_0-1}=u^I_{-N_0-1},$$

$$u^{II}_{N_0}=u_{N_0},$$

$$u^{II}_{N_0+1}=u_{N_0+1}.$$

The last three equations received from the motion equation for the atoms $n=\pm N_0$ and $n=N_0+1$ in the same manner.

After substitution of $u_n^{I\,IIint}$ from Eq. (7) and elimination of $U_{\pm Q}$, we find

$$\begin{aligned}
&-\cos QN_0[U^I_q e^{ip(N_0+1)}+U^I_{-q}e^{-ip(N_0+1)}\\
&\quad+U^{II}_q e^{-ip(N_0+1)}+U^{II}_{-q}e^{ip(N_0+1)}]\\
&\quad=\cos Q(N_0+1)[U^I_q e^{ipN_0}+U^I_{-q}e^{-ipN_0}\\
&\quad+U^{II}_q e^{-ipN_0}+U^{II}_{-q}e^{ipN_0}],\\
&-\sin QN_0[-U^I_q e^{ip(N_0+1)}-U^I_{-q}e^{-ip(N_0+1)}\\
&\quad+U^{II}_q e^{-ip(N_0+1)}+U^{II}_{-q}e^{ip(N_0+1)}]\\
&\quad=\sin Q(N_0+1)[-U^I_q e^{ipN_0}-U^I_{-q}e^{-ipN_0}\\
&\quad+U^{II}_q e^{-ipN_0}+U^{II}_{-q}e^{ipN_0}].
\end{aligned}$$

Here $p=\pi-q\ll 1$. This allows us to expand the exponents and rewrite the last equation as the boundary conditions (9) for $u_n^{I,II}(0)=U_q^{I,II}+U_{-q}^{I,II}$ and $\partial_n u_n^{I,II}(0)=-ip(U_q^{I,II}-U_{-q}^{I,II})$, which are the displacements and their derivatives at $n=0$. It can be shown that $\det\|t_{ik}\|=1$. In particular, for $Q=\pi$ (this happens when $\omega_D=\Omega_D$ in Fig. 3), we have $t_{11}=t_{22}=1$ and $t_{12}=t_{21}=0$.

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