

Propagation of nonequilibrium phonons in ceramic materials

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Phonon transport in single-phase ceramic materials is studied theoretically and experimentally. A simple equation for phonon transport is derived under the assumption that phonons propagate ballistically inside grains. It is shown that the effective phonon diffusion coefficient or the thermal conductivity is very sensitive to the manner in which the phonons pass through the contact region between neighboring grains. The arrival time of the peak value of the signal when a heat pulse is excited in the case of weak phonon nonequilibrium can be either an increasing or a decreasing function of the generator temperature. The temperature dependence of the low-temperature thermal conductivity in such ceramics should differ substantially from the T^3 law. Both possible types of behavior have been observed in experiments with propagation of heat pulses.

1. INTRODUCTION

It is well known that the elastic and thermal properties of microscopically inhomogeneous materials are substantially different from those of homogeneous materials.^{1,2} These differences are primarily associated with the structure of the material. Porosity, the size distribution of the microscopic particles (grains), and the properties of grain boundaries and contact regions between microparticles play the determining role in ceramics. The present paper is concerned with single-phase ceramics.

Vibrational excitations in ceramic materials in the long-wavelength region of the spectrum $\lambda \gg R$ (λ is the wavelength and R is the average size of the microparticles) are ordinary phonons, i.e., weakly damped plane waves. The damping is associated with scattering by microscopic inhomogeneities (as a rule, pores) and increases with decreasing wavelength according to the Rayleigh law $\Gamma \sim \lambda^{-4}$. The short-wavelength part of the spectrum of excitations with $\lambda \ll R$ is analogous to the spectrum of vibrational excitations of the material of the ceramic particles.

The excitation spectrum in the transitional region, i.e., the frequency range where the wavelength λ computed formally in terms of some average sound velocity is found to be of order R , is more complicated. If the transformation of the spectrum is followed as the transitional region is approached from the short-wavelength side, then the increased complexity is associated with the increased role of size effects, which determine the character of vibrations with $\lambda \sim R$, as well as with an increase in the contribution of surface modes. When the transitional region is approached from the long-wavelength side, a sharp increase in the scattering results for $\lambda \sim R$ in the localization of vibrations.³ We note that surface vibrations in microscopic particles of the ceramic are one of the types of localized vibrations in the system under study. In contrast to aerogels,^{4,5} where the transitional (fractonic) region of the spectrum may turn out to be very extended and the density of vibrational states depends on the fractal properties of the structure, in typical ceramics with grain size $R \gg 1 \mu\text{m}$ the transitional region of the spectrum is not likely to extend deep into the microwave region.

The aim of the present work is to investigate theoretically and experimentally the transport of vibrational excitations in ceramic materials. We discuss the lattice thermal

conductivity and propagation of heat pulses. Under experimental conditions in the temperature range $T \gg 1 \text{ K}$ the characteristic wavelength of the vibrations is at least one to two orders of magnitude smaller than R . Thus the transport processes are determined by excitations of the "particle" section of the vibrational spectrum of the ceramic, i.e., by phonons, just as in a continuous medium consisting of the ceramic material.

2. MODEL OF PHONON TRANSPORT IN CERAMIC MATERIALS

The propagation of nonequilibrium phonons (NEPs) in single-phase ceramic materials is determined not only by the properties of the material from which the ceramic is prepared, but also to a significant degree by the phonon transport through the contact regions (connecting necks) between the particles (grains) of the ceramic. If the area of the necks per particle is small compared with the area of the surface of a particle or transfer from one particle to another is inhibited for other reasons, then energy transport in the sample will be slow, even if inside each particle phonons move along ballistic trajectories.

In what follows we shall study the propagation of weakly nonequilibrium phonons, generated by a "warm" generator $\Delta T/T \ll 1$, where ΔT is the amount by which the temperature of the generator exceeds the temperature of the thermostat T . This makes it possible to neglect completely the anharmonic interactions in the ceramic material, which at low temperatures $T \leq 4.2 \text{ K}$ are characterized by relaxation times $\tau_r > 1\text{--}10 \text{ ms}$. In the samples employed, most of the energy in a heat pulse arrives at the bolometer over a time on the order of hundreds of microseconds, which is obviously shorter than the characteristic inelastic relaxation times τ_i . The spectral composition of a heat pulse can change as a result of inelasticity of phonon scattering near grain boundaries. If the total area of the contact boundaries is small compared with the area of a particle, then a phonon undergoes many collisions with the boundaries before it leaves the particle. Thus, even if the fraction of inelastic events of reflection from the boundaries is small, appreciable thermalization of the phonon gas inside each microparticle is possible. For this reason, we examine two limiting cases.

A. Thermalization of phonons in the boundary regions is insignificant

In this case the propagation of NEPs in thin ceramic samples occurs with conservation of the number of phonons and the spectral distribution of the injected phonons, i.e., the total number of phonons falling within the spectral interval from ω to $\omega + d\omega$ is an integral of the motion.

B. Thermalization in each microscopic particle is significant

The phonon distribution is in local equilibrium and the distribution parameter (temperature) depends on the location of the microscopic particle and the time.

We first study qualitatively the propagation of NEPs in a ceramic.

Suppose that each particle of the ceramic is, on the average, in contact with δ other particles. For close packing we have $\delta \gg 1$. The average area of all connecting necks per particle is equal to $\Sigma = \delta\sigma$, where σ is the average area of one neck. We assume that phonon reflection from sections of the particle surfaces which lie adjacent to pores is diffuse. There are two possible cases:

1) Phonon motion inside the particles is ballistic. If l is the mean-free path in the ceramic material, then we have $l > R$. Due to the technological idiosyncracies of the preparation of a ceramic, even in pure materials l can differ appreciably from the corresponding quantity characteristic for a single crystal at the same temperature.

2) Phonon motion inside particles is diffusive; i.e., $l < R$.

In our ceramics the quantity R is less than $10 \mu\text{m}$. Thus we assume that both cases are important and we study them separately.

Let t_0 be the characteristic residence time of a phonon in a given particle. After a time t_0 has elapsed, the phonon, with high probability, leaves the particle in which it was located and enters one of the neighboring particles which are in contact with the initial particle. In the process, the phonon migrates in space along one of the possible directions by an amount $\sim R$. This picture of the motion is similar to the hopping mechanism by which excitations are transported. Here R plays the role of the hopping length and t_0 is the characteristic hopping time. For time scales $t \gg t_0$, this process is described by a diffusion equation, and the diffusion coefficient is

$$D \sim \frac{R^2}{t_0}.$$

If the phonon motion inside a particle with $l > R$ is ballistic (case 1), then, evidently,

$$t_0 \propto \frac{RS}{v_s \Sigma f_\omega},$$

where S is the average surface area of a particle and

$$D \propto v_s R \frac{\Sigma}{S} f_\omega.$$

Here the factor f_ω is the probability that a phonon passes along the connecting neck from one particle into another. Generally speaking, this quantity depends on the wavelength (energy) of the incident phonon. Thus, in the first case, the bolometer signal reaches its peak value at the time

$$t_m^{(1)} \sim \frac{L^2}{D} \sim \frac{L^2}{v_s R f_\omega} \frac{S}{\Sigma},$$

where L is the length of the sample.

In the second case the time t_0 can be estimated as follows. The time t_1 required in order for a phonon to diffuse to the surface of a particle is of order R^2/D_1 . Here D_1 is the phonon diffusion coefficient in the particle. If, in the process, the phonon reaches the connecting neck, then it exits with probability f_ω into the neighboring particle. Thus the scale t_0 is equal to

$$t_0 \sim t_1 \frac{S}{\Sigma} \frac{1}{f_\omega},$$

and the signal peak arrives at the bolometer at the time

$$t_m^{(2)} \sim \frac{L^2 t_0}{R^2} \sim \left(\frac{L}{R} \right)^2 \frac{R^2}{D_1} \frac{S}{\Sigma} \frac{1}{f_\omega} \sim \frac{L^2}{D_1} \frac{S}{\Sigma} \frac{1}{f_\omega}.$$

The meaning of this result is obvious. The effective diffusion coefficient in a porous ceramic material is less than the diffusion coefficient in a continuous material by the amount of the multiplier $\Sigma f_\omega / S$, describing the decrease in the probability of spatial migration of a phonon in connection with the requirement that the phonon pass through the neck (compare Ref. 6).

The foregoing analysis obviously refers to the case A. We note that similar arguments can be used even in the case B, if the change in the energy of the phonon gas in the chosen microparticle is studied instead of the change in the number of phonons in the particle and the phonon energy flux through the contact region is studied instead of the phonon flux through the contact region.

3. PROPAGATION OF NEPs IN CERAMICS

1. Suppose the thermalization of NEPs in the ceramic is insignificant. Let $N(\mathbf{r}_v, t)$ be the phonon number density at frequency ω (for simplicity we omit this dependence) in a particle with coordinate \mathbf{r}_v at time t . On the basis of the assumption that phonon reflection from the boundaries of a particle with pores is diffuse and also since

$$\frac{\Sigma}{S} f_\omega \ll 1,$$

any nonuniform phonon distribution inside a particle becomes rapidly uniform (over a time of the order of $R/v_s \ll t_0$). Thus we assume that the phonon density inside each particle is uniform. The quantity $N(\mathbf{r}_v, t)$ evidently satisfies the continuity equation, which we write in the form

$$\frac{\partial N(\mathbf{r}_v, t)}{\partial t} = - \sum_{v'} [p(v \rightarrow v') N(\mathbf{r}_v, t) - p(v' \rightarrow v) N(\mathbf{r}_{v'}, t)]. \quad (1)$$

Here $p(v \rightarrow v')$ is the probability per unit time of a transition phonon from particle v into a particle v' , in contact with the particle v , when the phonon is incident on the connecting neck between the particles; the summation in Eq. (1) extends over all particles v' in contact with the given particle v . In accordance with the foregoing discussion, in the formula (1) no distinction is made between the phonon densities near the neck and in the volume of the particle.

In order to elucidate the meaning of the quantity

$p(v \rightarrow v')$, we write the balance of phonon transitions through the contact region σ per unit time, using the assumption that phonon reflection from the boundaries is diffuse. Then the number of phonons passing per unit time from the v th microparticle into the v' th microparticle and vice versa, can be written in exactly the same way as if the phonons passed through the contact area σ from one half-space with phonon density n_v into another half-space with density $n_{v'}$.

In this case we have instead of Eq. (1)

$$\frac{\partial N(\mathbf{r}_v, t)}{\partial t} = -\frac{1}{4} \frac{v_s f_\omega}{V} \sum_v \sigma_{v,v'} [N(\mathbf{r}_v, t) - N(\mathbf{r}_{v'}, t)],$$

where V is the volume of the v th microparticle and $\sigma_{v,v'}$ is the area of the contact region connecting the v th and v' th microparticles. Thus

$$p(v \rightarrow v') = \frac{1}{4} \frac{v_s f_\omega \sigma_{v,v'}}{V} \approx \frac{\sigma}{S} \frac{v_s}{R} f_\omega.$$

Evidently,

$$\sum_{v'} p(v \rightarrow v') \approx \delta p(v \rightarrow v') = \delta \frac{\sigma}{S} \frac{v_s}{R} f_\omega = \frac{\Sigma}{S} \frac{v_s}{R} f_\omega \sim \frac{1}{t_0}.$$

Assuming that $N(\mathbf{r}_v, t)$ is a continuously varying function of position, we expand the function $N(\mathbf{r}_{v'}, t)$ in a series in powers of $\mathbf{r}_{v'} - \mathbf{r}_v$. Such an expansion is valid, if $N(\mathbf{r}_v, t)$ varies significantly over a distance appreciably greater than the grain size R . Thus we obtain

$$\frac{\partial N(\mathbf{r}_v, t)}{\partial t} = - \sum_{v'} (\mathbf{a}_{vv'} \cdot \nabla N(\mathbf{r}_v, t) + {}^{1/2} (\mathbf{a}_{vv'} \cdot \nabla)^2 N(\mathbf{r}_v, t)) p(v \rightarrow v'), \quad (2)$$

where we have introduced

$$\mathbf{a}_{vv'} = \mathbf{r}_{v'} - \mathbf{r}_v$$

is the radius vector from the center of the v th particle to the center of the v' th particle.

In writing down Eq. (2) we assumed that the probabilities of a transition from v into v' and from v' into v through the contact area are equal to one another, i.e.,

$$p(v \rightarrow v') = p(v' \rightarrow v).$$

We introduce the vector

$$\mathbf{V}(\mathbf{r}_v) = \sum_{v'} p(v \rightarrow v') \mathbf{a}_{vv'}$$

and the quantity

$$D(\mathbf{r}_v) = {}^{1/6} \sum_{v'} p(v \rightarrow v') \mathbf{a}_{vv'}^2.$$

The equation (2) can now be rewritten in the form

$$\begin{aligned} & \frac{\partial N(\mathbf{r}_v, t)}{\partial t} - (\mathbf{V}(\mathbf{r}_v) \cdot \nabla) N(\mathbf{r}_v, t) - D(\mathbf{r}_v) \Delta N(\mathbf{r}_v, t) \\ & = \frac{1}{2} \sum_{v'} \left[(\mathbf{a}_{vv'} \cdot \nabla)^2 - \frac{1}{3} a_{vv'}^2 \Delta \right] p(v \rightarrow v') N(\mathbf{r}_v, t). \end{aligned} \quad (3)$$

Let $\langle A(\mathbf{r}_v) \rangle$ denote the statistical average of the quantity $A(\mathbf{r}_v)$ over the distribution of microparticles of the ceramic.

Let

$$D \equiv \langle D(\mathbf{r}) \rangle.$$

Writing

$$d(\mathbf{r}_v) \equiv D(\mathbf{r}_v) - D,$$

we obtain from Eq. (3)

$$\begin{aligned} \frac{\partial N(\mathbf{r}_v, t)}{\partial t} - D \Delta N(\mathbf{r}_v, t) = & \left[(\mathbf{V}(\mathbf{r}_v) \cdot \nabla) + d(\mathbf{r}_v) \Delta \right. \\ & \left. + {}^{1/2} \sum_{v'} \left[(\mathbf{a}_{vv'} \cdot \nabla)^2 - \frac{1}{3} a_{vv'}^2 \Delta \right] p(v \rightarrow v') \right] N(\mathbf{r}_v, t). \end{aligned} \quad (4)$$

We introduce the operator

$$\begin{aligned} \bar{L}(\mathbf{r}_v) \equiv & (\mathbf{V}(\mathbf{r}_v) \cdot \nabla) + d(\mathbf{r}_v) \Delta \\ & + {}^{1/2} \sum_{v'} \left[(\mathbf{a}_{vv'} \cdot \nabla)^2 - \frac{1}{3} a_{vv'}^2 \Delta \right] p(v \rightarrow v'). \end{aligned}$$

We now perform the statistical averaging in Eq. (4). Let

$$n(\mathbf{r}, t) \equiv \langle N(\mathbf{r}, t) \rangle.$$

We obtain

$$\frac{\partial n(\mathbf{r}_v, t)}{\partial t} - D \Delta n(\mathbf{r}_v, t) = \langle \bar{L}(\mathbf{r}) N(\mathbf{r}, t) \rangle. \quad (5)$$

The equation for the Fourier transform $n(\mathbf{r}, \omega)$ has the form

$$(-i\omega - D\Delta) n(\mathbf{r}, \omega) = \langle \bar{L}(\mathbf{r}) N(\mathbf{r}, \omega) \rangle. \quad (6)$$

If $G(\mathbf{r}, \omega)$ is the Green's function for the diffusion equation with a point source, then substituting the formal solution of Eq. (4) into the right-hand side of Eq. (6) gives

$$(-i\omega - D\Delta) n(\mathbf{r}, \omega) = \int d\mathbf{r}' \langle \bar{L}(\mathbf{r}) G(\mathbf{r} - \mathbf{r}', \omega) \bar{L}(\mathbf{r}') N(\mathbf{r}', \omega) \rangle. \quad (7)$$

We introduce on the right-hand side of Eq. (7) a planar source of phonons, which injects phonons into the sample at time $t = 0$ from the plane $z = 0$:

$$\begin{aligned} (-i\omega - D\Delta) n(\mathbf{r}, \omega) = & \frac{a}{2\pi} \delta(z) \\ & + \int d\mathbf{r}' \langle \bar{L}(\mathbf{r}) G(\mathbf{r} - \mathbf{r}', \omega) \bar{L}(\mathbf{r}') N(\mathbf{r}', \omega) \rangle. \end{aligned} \quad (8)$$

Here $a \equiv a(\omega)$ is the spectral distribution of the injected phonons. We perform the averaging in Eq. (8), decoupling the average in the integrand. We obtain

$$\begin{aligned} (-i\omega - D\Delta) n(\mathbf{r}, \omega) = & \frac{a}{2\pi} \delta(z) \\ & + \int d\mathbf{r}' \langle \bar{L}(\mathbf{r}) G(\mathbf{r} - \mathbf{r}', \omega) \bar{L}(\mathbf{r}') n(\mathbf{r}', \omega) \rangle. \end{aligned} \quad (9)$$

We now transform the integrand in Eq. (9), introducing the Fourier transforms $G(\mathbf{k}, \omega)$ and $n(\mathbf{k}, \omega)$:

$$\langle \hat{L}(\mathbf{r}) G(\mathbf{r}-\mathbf{r}', \omega) \hat{L}(\mathbf{r}') n(\mathbf{r}', \omega) \rangle = \int d\mathbf{q}_1 d\mathbf{q}_2 G(\mathbf{q}_1, \omega) n(\mathbf{q}_2, \omega) \times \langle \hat{L}_{\mathbf{q}_1}(\mathbf{r}) \hat{L}_{\mathbf{q}_2}(\mathbf{r}') \rangle \exp[i\mathbf{q}_1(\mathbf{r}-\mathbf{r}') + i\mathbf{q}_2\mathbf{r}']. \quad (10)$$

Here

$$L_{\mathbf{q}}(\mathbf{r}) \equiv i\mathbf{q}\mathbf{V}(\mathbf{r}) - q^2 d(\mathbf{r}) - 1/2 \sum_{\nu'} [(a_{\nu\nu}, \mathbf{q})^2 - 1/3 a_{\nu\nu}^2 q^2] p(\nu \rightarrow \nu').$$

In a macroscopically homogeneous medium the quantity $\langle \hat{L}_{\mathbf{q}_1}(\mathbf{r}) \hat{L}_{\mathbf{q}_2}(\mathbf{r}') \rangle$ depends on the difference $\mathbf{r} - \mathbf{r}'$. We introduce the notation

$$L_{\mathbf{q}_1, \mathbf{q}_2}^z(\mathbf{r}-\mathbf{r}') \equiv \langle L_{\mathbf{q}_1}(\mathbf{r}) L_{\mathbf{q}_2}(\mathbf{r}') \rangle.$$

Fourier transforming Eq. (9) with respect to the spatial variable we obtain

$$(-i\omega + Dk^2) n(\mathbf{k}, \omega) = \frac{a}{(2\pi)^2} \delta(k_x) \delta(k_y) + (2\pi)^3 \int d\mathbf{q} G(\mathbf{q}, \omega) L_{\mathbf{q}\mathbf{k}}^z(\mathbf{q}-\mathbf{k}) n(\mathbf{k}, \omega). \quad (11)$$

Finally

$$n(\mathbf{k}, \omega) = \frac{a}{(2\pi)^2} \frac{\delta(k_x) \delta(k_y)}{-i\omega + Dk^2 - (2\pi)^3 \int d\mathbf{q} G(\mathbf{q}+\mathbf{k}, \omega) L_{\mathbf{q}+\mathbf{k}, \mathbf{k}}^z(\mathbf{q})}. \quad (12)$$

We now examine

$$\int d\mathbf{q} G(\mathbf{q}+\mathbf{k}, \omega) L_{\mathbf{q}+\mathbf{k}, \mathbf{k}}^z(\mathbf{q}).$$

We are interested in $n(\mathbf{k}, \omega)$ in the long-wavelength limit, since

$$|\mathbf{k}| \sim k_z \sim \frac{1}{L}.$$

It is easy to verify that the integration in the region

$$q \gg k \sim 1/L$$

makes the main contribution to the integration. This means that we can perform the integration by expanding the integrand in a series in the small parameter

$$\frac{k}{q} \ll 1$$

and retain only the terms of lowest order in k/q .

We now examine in greater detail

$$\begin{aligned} L_{\mathbf{q}+\mathbf{k}, \mathbf{k}}(\mathbf{r}-\mathbf{r}') &\equiv -\langle (\mathbf{q}+\mathbf{k}, \mathbf{V}(\mathbf{r})) (\mathbf{k}, \mathbf{V}(\mathbf{r}')) \rangle \\ &+ (\mathbf{q}+\mathbf{k})^2 k^2 \langle d(\mathbf{r}) d(\mathbf{r}') \rangle \\ &+ 1/2 \sum_{\nu, \mu'} [(a_{\nu\nu}, \mathbf{q}+\mathbf{k})^2 - 1/3 a_{\nu\nu}^2 (\mathbf{q}+\mathbf{k})^2] [(a_{\mu\mu}, \mathbf{k})^2 \\ &- 1/3 a_{\mu\mu}^2 k^2] p(\nu \rightarrow \nu') p(\mu \rightarrow \mu'). \end{aligned}$$

Here $\mathbf{r}_\nu \rightarrow \mathbf{r}$ and $\mathbf{r}_\mu \rightarrow \mathbf{r}'$. In writing this equality we employed the expression for $L_{\mathbf{q}}(\mathbf{r})$, the fact that

$$\langle \mathbf{V}(\mathbf{r}) \rangle = 0$$

and

$$\langle d(\mathbf{r}) \rangle = \left\langle \sum_{\nu'} [(a_{\nu\nu}, \mathbf{q})^2 - 1/3 a_{\nu\nu}^2 q^2] p(\nu \rightarrow \nu') \right\rangle = 0.$$

In a macroscopically isotropic medium

$$\langle (\mathbf{q}+\mathbf{k}, \mathbf{V}(\mathbf{r})) (\mathbf{k}, \mathbf{V}(\mathbf{r}')) \rangle = (k^2 + \mathbf{k}\mathbf{q}) \langle \mathbf{V}(\mathbf{r}), \mathbf{V}(\mathbf{r}') \rangle.$$

The second and third terms in the expression for $L_{\mathbf{q}+\mathbf{k}, \mathbf{k}}(\mathbf{r}-\mathbf{r}')$ are proportional to k^2 and give on integration over $d\mathbf{q}$ an insignificant renormalization of the diffusion coefficient D .

Integrating the remaining terms in $L_{\mathbf{q}+\mathbf{k}, \mathbf{k}}(\mathbf{r}-\mathbf{r}')$ and retaining only the contribution of lowest order in $k/q \ll 1$, we obtain after substitution into Eq. (12)

$$n(\mathbf{k}, \omega) = \frac{a}{(2\pi)^3} \frac{\delta(k_x) \delta(k_y)}{-i\omega + k^2 (D + 1/3 R_0^2 v_0^2 / D)}. \quad (13)$$

Here

$$R_0^2 \equiv \frac{1}{(2\pi)^2} \frac{\int_0^\infty d\mathbf{q} v_0^2(\mathbf{q})}{\int_0^\infty d\mathbf{q} q^2 v_0^2(\mathbf{q})}$$

is the correlation radius and

$$v_0^2 \equiv \int d\mathbf{q} v^2(\mathbf{q}) \equiv \langle \mathbf{V}(\mathbf{r}) \mathbf{V}(\mathbf{r}') \rangle.$$

Thus in the case at hand the propagation of NEPs in the ceramic is described by the one-dimensional diffusion equation with effective diffusion coefficient

$$D_{\text{eff}} \equiv D + \frac{1}{3} \frac{v_0^2 R_0^2}{D}. \quad (14)$$

We now make a number of estimates. In order of magnitude we have $D \sim \delta p R^2$, where δ is the average number of particles in contact with the selected particle, p is the average transmission factor of the connecting neck, R^2 is the mean-square radius of the particle, $v_0^2 \sim (\delta^{1/2} p R)^2 = \delta p^2 R^2$, if it is assumed that $\delta \gg 1$, and $\delta^{1/2}$ characterizes the scale of the fluctuations in the number of particles in contact near the mean value.

Thus the ratio of the first and second terms is of the order of $(R_0/R)^2/\delta$. Depending on the ratio of R_0 and R , this quantity can be either less or greater than unity. The significance of the quantity R_0 evidently lies in the fact that in a region of characteristic size R_0 phonons move from particle to particle along a preferred direction. For $R_0 \sim R$, we have $D_{\text{eff}} \approx D$ and the second term makes only an insignificant correction to the average diffusion coefficient. This is probably the situation in homogeneous ceramics with a small spread of the particle radii near the average radius (Fig. 1). Conversely, in ceramics where small particles fill the gap between larger particles, i.e., ceramics with a larger spread of the particle radii, the quantity R_0/R can be quite

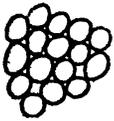


FIG. 1. Structure of ceramic with low particle-size variance.

large (Fig. 2). For example, for all small particles which are in contact with a large particle the quantity \mathbf{V} is directed toward the large particle and the correlation radius R_0 reaches the radius of the large particle.

The origin of the term $v_0^2 R_0^2 / D$ has a simple meaning. Indeed, consider the plane $z = \text{const}$, near which a large particle is in contact with a collection of small particles. If the small particles with radius r in this plane were in contact with small particles lying near the planes $z \pm r$, then the balance of phonon transitions between particles would be determined by the small difference in the phonon density in neighboring particles. In the case of contact with a large particle, the difference between the average phonon density inside each particle and the average phonon density in the plane $z = \text{const}$ is greater because it is determined by the average phonon density between the planes $z = \text{const}$ and $z = \text{const} + R$, since irrespective of the distribution of sources of the entering phonons, after a time of the order of R/v_s has elapsed the phonon density inside a particle becomes uniform as a result of diffuse scattering of phonons at the boundary. The jump $N(\mathbf{r}_v) - N(\mathbf{r}_{v'})$ arising in the case of contact between small particles and a large particle is much larger than in the case of contact between identical particles both in the plane $z = \text{const}$ and in the plane $z = \text{const} + R$. This means that passage through a region with volume R_0^3 in the presence of large particles occurs much more quickly. The diffusion process in such a ceramic may be significantly more rapid than the diffusion process in a weakly inhomogeneous ceramic with a small spread in the particle radii and the same average grain size.

The arrival time of the signal peak at the bolometer is determined by the expression $t_m \sim L^2 / D_{\text{eff}}$. In a weakly inhomogeneous ceramic $D \gg v_0^2 R_0^2 / D$ and $t_m \sim L^2 / D \sim L^2 / \delta p R^2$, and we obtain for t_m an expression that is identical to the result of qualitative analysis.

2. We now examine the other limiting case, assuming the number of reflections of a phonon from intergrain boundaries $v_s t_0 / R \gg 1$ and, in addition, $\xi v_s t_0 / R \gg 1$, where ξ is the inelasticity parameter for phonon scattering at the bound-

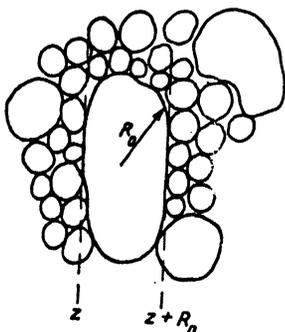


FIG. 2. Structure of ceramic with high particle-size variance.

ary. On the basis of the last inequality it can be assumed that a locally equilibrium phonon distribution is established inside each microparticle of the ceramic; i.e., the phonon distribution function has the form $n(\mathbf{r}_v, t) = 1 / \exp[\hbar\omega / k_B T(\mathbf{r}_v, t)]^{-1}$. In this case, instead of the equation (1), which expresses the law of conservation of the number of phonons with energies from ω to $\omega + d\omega$, we can write the continuity equation for the energy. Let $E(\mathbf{r}_v, t) = \int_v d\mathbf{r} \int_0^\infty d\omega \hbar\omega \rho(\omega) n(\omega; \mathbf{r}_v, t)$ be the energy of the gas of nonequilibrium phonons in the v th microparticle. Then, evidently,

$$\frac{\partial E(\mathbf{r}_v, t)}{\partial t} = - \sum_{v'} \int_0^\infty d\omega \rho(\omega) \tilde{p}_\omega(v \rightarrow v') \times \hbar\omega [n(\omega; \mathbf{r}_v, t) - n(\omega; \mathbf{r}_{v'}, t)], \quad (15)$$

where, as before, $\tilde{p}_\omega(v \rightarrow v') \sim (\sigma/S)(v_s/R)f_\omega$. The right-hand side of Eq. (15) is the difference of the energy fluxes of nonequilibrium phonons flowing through the contact regions between the v th particle and all neighboring particles.

Setting $n(\omega; \mathbf{r}_v, t) - n(\omega; \mathbf{r}_{v'}, t) \approx -(\partial n / \partial T) [T(\mathbf{r}_{v'}) - T(\mathbf{r}_v)] \approx (\partial n / \partial T) [(\mathbf{a}_{vv'} \cdot \nabla) + \frac{1}{2}(\mathbf{a}_{vv'} \cdot \nabla)^2] T(\mathbf{r}_v, t)$ and $\partial E / \partial t = (\partial E / \partial T)(\partial T / \partial t) = C_v(\partial T / \partial t)$, where C_v is the specific heat capacity of the ceramic material, we obtain finally

$$\frac{\partial T(\mathbf{r}_v, t)}{\partial t} = \sum_{v'} \tilde{p}(v \rightarrow v') \left[(\mathbf{a}_{vv'} \cdot \nabla) + \frac{1}{2}(\mathbf{a}_{vv'} \cdot \nabla)^2 \right] T(\mathbf{r}_v, t), \quad (16)$$

which differs from Eq. (2) only by other quantities $\tilde{p}(v \rightarrow v')$, describing some average transition probability between the v th and v' th microparticles:

$$\tilde{p}(v \rightarrow v') \equiv \frac{\int_0^\infty d\omega \rho(\omega) \tilde{p}_\omega(v \rightarrow v') \hbar\omega \frac{\partial n}{\partial T}}{\int_0^\infty d\omega \rho(\omega) \hbar\omega \frac{\partial n}{\partial T}}$$

The further analysis of the solution of Eq. (15) is completely similar to the analysis presented above for the case when appreciable thermalization of NEPs does not occur. The obvious difference lies only in the fact that the expression for the effective diffusion coefficient is different: $\tilde{p}(v \rightarrow v')$ appears instead of $p(v \rightarrow v')$.

We now examine the question of the temperature dependence of the arrival time t_m of the signal peak. In the expression (14) for D_{eff} the only quantity that can depend on the phonon wavelength is, evidently, the quantity p ; both terms in D_{eff} are proportional to p (in the second term $v_0^2 \sim p^2$ and D in the denominator is proportional to p). Thus $t_m \sim 1/p\bar{\omega}$, where $\bar{\omega}$ is the average frequency of the injected phonons. There are several possible cases.

1. Phonon transmission through a connecting neck is described by the theory of acoustic matching. In this case the transmission factor f does not depend on the frequency (wavelength) of the phonon. Thus $t_m(T) = \text{const}$ and the

arrival time of the signal peak is independent of the temperature.

2. A specific dependence of the transmission factor f_ω on the phonon frequency (wavelength) can arise if the characteristic linear size r_0 of the contact region is small and comparable to the phonon wavelength. In this case phonon transmission through the connecting neck is determined by diffraction of phonons. Assuming that the neck is small compared to the radius of the particle, the well-known result for the diffraction of a wave by a round opening in a flat screen can be used. If $\lambda \gg r_0$ holds, then f_ω follows the Rayleigh law $f_\omega \sim \omega^4$. In any case, as the temperature increases and the average wavelength of NEPs decreases the transmission factor f_ω increases and t_m decreases; i.e., $\partial t_m / \partial T < 0$.

3. If $r_0 \gg \lambda$ holds, then the frequency dependence f_ω can arise if a large number of defects is concentrated in the region of the connecting neck. There is nonetheless a possibility that a phonon approaching a neck in the required direction will be reflected backward into the initial particle. If the phonon scattering cross section of defects in the region of a neck increases with increasing average frequency of the NEPs, then as the temperature increases the quantity p_ω decreases and t_m increases: $\partial t_m / \partial T > 0$.

4. The character of phonon transmission from one particle to another can be determined by the fractal structure of the connecting neck. If the characteristic phonon frequency in the heat pulse ($\nu \sim 0.1$ THz) corresponds to the fracton region of the spectrum of excitations in connecting necks, then excitation transfer in a neck can be associated with a hopping mechanism. Under these conditions the probability f_ω that a phonon incident on a neck is transmitted from one particle to another depends on the temperature and increases with increasing temperature, since the process is activational. The increase in f_ω with increasing temperature results in an increase of the effective diffusion coefficient. Under these conditions $\partial t_m / \partial T < 0$.

Thus, depending on the type of ceramic the following cases are possible under conditions of ballistic propagation of phonons in ceramic particles: $t_m(T) = \text{const}$, $\partial t_m / \partial T < 0$, and $\partial t_m / \partial T > 0$.

An unusual temperature dependence of t_m with $\partial t_m / \partial T < 0$ can also arise for reasons unrelated with phonon diffraction by connecting necks or the fractal character of the necks. The following discussion illustrates this. Consider the expression (14). Suppose that the quantity D depends on the temperature. This could be associated, for example, with the neglected contribution of phonon diffusion within a particle of the ceramic. It is obvious that the structural contribution to D_{eff} , i.e., the term $v_0^2 R_0^2 / D$, will remain in any case, since this term takes into account the possibility of "fast" diffusion within regions of size $\sim R_0$ in an inhomogeneous ceramic. Thus the temperature dependence $D_{\text{eff}}(T)$ is determined either by $D(T)$, if we have $D(T) > v_0 R_0$, or $v_0^2 R_0^2 / D(T)$, if we have $D(T) < v_0 R_0$, and if $D(T)$ decreases with increasing T , then it is possible to have a case when $\partial t_m / \partial T$ changes sign. Let T_0 be the temperature determined from the condition $D(T_0) = v_0 R_0$. For $T < T_0$ we have $\partial t_m / \partial T > 0$; for $T > T_0$ we have, conversely, $\partial t_m / \partial T < 0$.

We now briefly discuss the behavior of the low-temperature thermal conductivity of a ceramic. Let T_R be the temperature determined from the condition $\lambda \approx R$. In the

region $T > T_R$, evidently, $\lambda < R$ holds and phonon localization effects³ can be neglected. Since we are considering a model of phonon transport which presupposes that $\lambda \ll R$, we confine our attention to the case $T > T_R$. It is convenient to use the results of analysis for case B. Actually, after statistical averaging the equation (16) can be transformed (similarly to Eq. (1) in the A) to the equation for thermal conductivity. In order to make a qualitative assessment we can employ the relation

$$\kappa \sim C_v D_{\text{eff}}.$$

The temperature dependence of the thermal conductivity $\kappa(T)$ at low temperatures is determined by the temperature dependence of $C_v(T) \sim T^3$ as well as by the temperature dependence of $D_{\text{eff}}(T)$. Thus, in the acoustic-matching model we have $D_{\text{eff}}(T) = \text{const}$ and $\kappa(T) \sim T^3$. In the case

$$\partial t_m / \partial T < 0$$

the effective diffusion coefficient $D_{\text{eff}}(T)$ increases with increasing temperature and $\kappa(T)/T^3$ is an increasing function of T . The temperature dependence of $\kappa(T)$ in such ceramics can contain a section with a sharper temperature dependence than T^3 . If we have

$$\partial t_m / \partial T > 0,$$

then $D_{\text{eff}}(T)$ decreases with increasing T , and in such ceramics, conversely, a section with a weaker temperature dependence than T^3 can appear in $\kappa(T)$.

At higher temperatures the proposed model of phonon transport is no longer applicable. The properties of contact regions no longer dominate, and irrespective of the type of regions $\kappa(T)$ follows the same law for ceramics with the same structure. Thus, depending on the properties of contact regions, for $T > T_R$ features in the form of steps or dips can appear in the curve $\kappa(T)$.

The possible temperature dependence $\kappa(T)$ in ceramic materials at low temperatures is shown schematically in Fig. 3.

We note that these features in $\kappa(T)$ can be deserved only if for the dominant group of phonons with characteristic frequencies $\omega_d(T)$, which determine $\kappa(T)$, the quantity D_{eff} depends on $\omega_d(T)$. In addition, evidently, the dominant phonon groups determining $\kappa(T)$ and $t_m(T)$ can be different. As a result, the features in $\kappa(T)$ can appear in a different temperature interval. In addition, the same contact can have



FIG. 3. Temperature dependence of the low-temperature thermal conductivity of ceramic materials: (1) $\partial t_m / \partial T = 0$, (2) $\partial t_m / \partial T < 0$, and (3) $\partial t_m / \partial T > 0$.

different properties for phonons with different frequencies. Thus a fractal or amorphized contact for transmission of long-wavelength phonons is described, evidently, by the theory of acoustic matching. From what we have said above it is obvious that a quantitative theory of the thermal conductivity of ceramic materials at temperatures $T > T_R$, as well as a comparison with experimental data, should be based on the possibility of a detailed description of the properties of the contact regions.

4. EXPERIMENT

The arrangement of the experiment is as follows. Thin, 100–200 μm thick, ceramic wafers were polished to optical quality. A thin ($\sim 1000 \text{ \AA}$ thick) film of gold, which was the injector of nonequilibrium phonons (NEPs), was deposited on one of the polished faces by the method of thermal sputtering. Weakly nonequilibrium phonons were excited in the samples; i.e., heating of the film with a current pulse made it possible to achieve conditions such that $\Delta T \ll T_0$, where $\Delta T = T_H - T_0$ and T_0 is the temperature of the thermostat. The phonon-nonequilibrium signal passing through the sample was recorded on the opposite face of the sample with a wideband bolometer based on a superconducting junction of In or Sn films. Displacement of the working point of the bolometer by a weak magnetic field made it possible to obtain the temperature dependence of the scattering of NEPs in the sample.⁷

For the object of investigation we chose well-known ceramics, produced commercially and widely employed in technology and differing significantly with respect to mechanical and physical properties and technology of preparation. These are the ceramics lead-lanthanum zirconate-titanate (LLZT) and 22KhS brand ruby ceramic.

The basic quantity measured in the experiment was the arrival time t_M of the peak value of the phonon-nonequilibrium signal and its dependence on the temperature and the structural characteristics of the sample.

The measurements were performed in the temperature range 2.2–3.8 K. The temperature of the heater exceeded the temperature of the thermostat by an amount $\leq 0.2 \text{ K}$. According to Ref. 7, this made it possible to obtain the temperature dependence $t_M(T)$ by changing the temperature of the



FIG. 5. Electron micrograph of a LLZT ceramic chip on which measurements were performed.

thermostat by changing the rate of pumping of helium vapors out of the cryostat.

The low temperatures of the experiment and the low energies of NEPs made it possible to eliminate from analysis the phonon-phonon interactions associated with weak anharmonicity of the lattice of the initial material and to assume that the recorded signal is the result of scattering of nonmonochromatic phonons, whose initial frequency distribution was close to the Planck distribution and which did not interact with one another, in the sample.

Figure 4 shows a series of the phonon-nonequilibrium signals $S(t)$, recorded by the bolometer, for the LLZT sample.

As expected, the curves have the bell shape, characteristic for diffusion propagation, with a pronounced maximum.

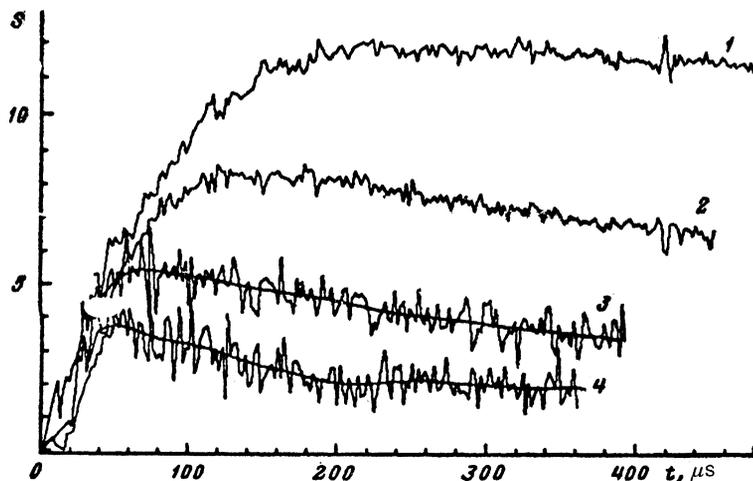


FIG. 4. Bolometer signals indicating phonon nonequilibrium in a LLZT sample with $L = 120 \mu\text{m}$. $T = 3.82$ (1), 3.4 (2), 3.01 (3), and 2.2 K (4).

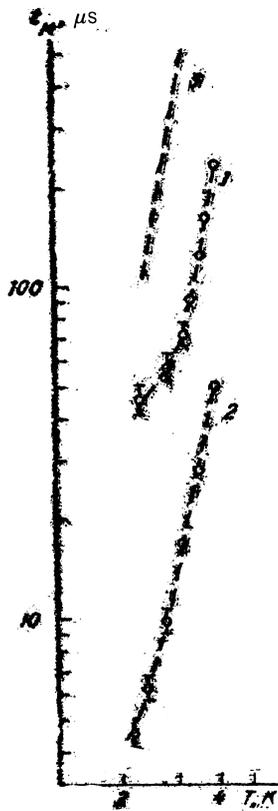


FIG. 6. Temperature dependence $t_M(T)$ for LLZT ceramic with (1) $L = 120 \mu\text{m}$, fused quartz with (2) $L = 160 \mu\text{m}$ with $P_H < 10^{-1} \text{ W/mm}^2$ and the temperature dependence (3) $t_M \sim T^5$.

The arrival time of the peak value decreased with the temperature (energy of NEPs); this corresponded to a decrease in the intensity of the scattering.

Figure 5 shows an electron micrograph of a chip of the sample measured; one can see that the average grain size is equal to $3\text{--}5 \mu\text{m}$ with comparatively close packing. The ceramic is transparent, and it does not contain any defects that can be seen with an optical or an acoustic microscope.

It is interesting that the temperature dependence satisfies

$$t_M(T) \sim T^n,$$

where $n \geq 5$. This eliminates the possibility of Rayleigh scattering of NEPs. At the same time, this temperature dependence is very similar to the temperature dependence $t_M(T)$ observed in glasses under the same experimental conditions.⁸

Figure 6 shows the temperature dependences $t_M(T)$ for LLZT and fused quartz.

$$t_M(L) \sim L^2$$

in both glasses and the ceramic materials studied. This corresponds to the conditions of diffusive propagation of NEPs, since

$$t_M \sim \frac{L^2}{v^2 \tau}.$$

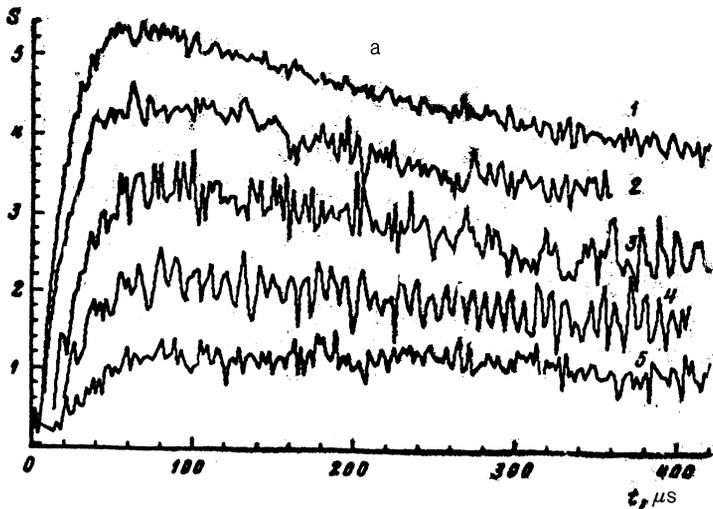
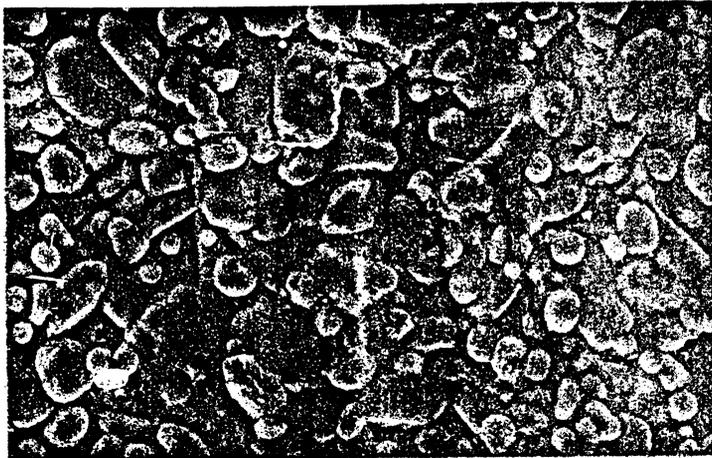


FIG. 7. a) Phonon-nonequilibrium signals for a sample of ruby ceramic. $L = 140 \mu\text{m}$, $P_H < 10^{-1} \text{ W/mm}^2$, $T = 3.8$ (1), 3.65 (2), 3.37 (3), 3.13 (4), and 2.44 K (5). b) Electron micrograph of the structure of the sample in Fig. 7a prior to mechanical treatment.



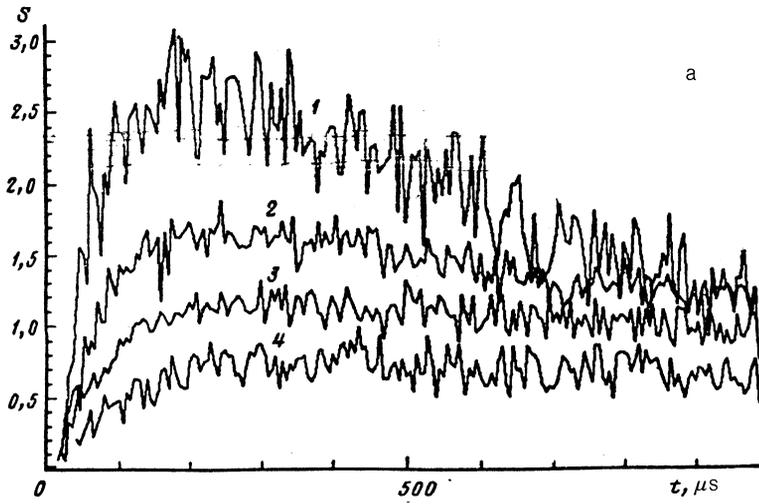


FIG. 8. a) Phonon-nonequilibrium signal for a sample of ruby ceramic. $L = 140 \mu\text{m}$, $P_H < 10^{-1} \text{ W/mm}^2$, $T = 3.78$ (1), 3.49 (2), 3.14 (3), and 2.46 K (4). b) Electron micrograph of the structure of the sample in Fig. 8a prior to mechanical treatment.

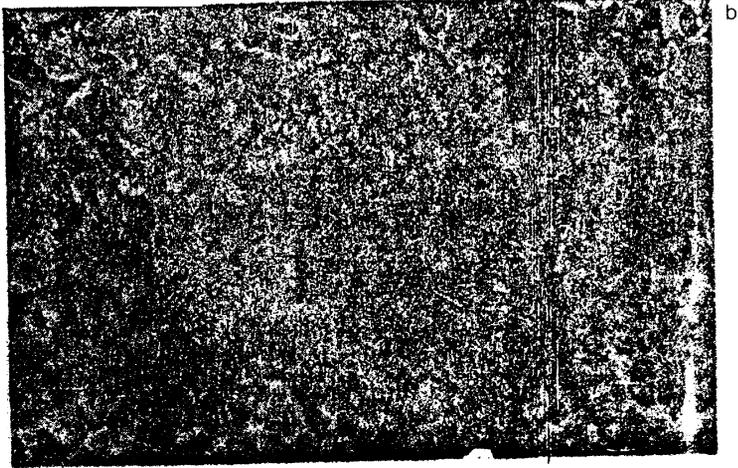


FIG. 9. Portion of Fig. 7b with strong magnification.

The weaker temperature dependence $t_M(T)$ with constant heating power P_H is the result of an increase in

$$\Delta T = T_H - T_0,$$

occurring as the temperature of the thermostat decreases, since

$$P_H \sim \alpha(T_H^4 - T_0^4) \sim \alpha T_0^3 \Delta T$$

for $\Delta T \ll T_0$ (the coefficient α is determined by the conditions of acoustic matching of the heater and the substrate). This effect can be taken into account in the manner described in Ref. 7.

The observed behavior of $T_M(T)$ in LLZT ceramics could indicate the existence of amorphized contact regions between microparticles of the ceramic, where the phonon transport process is similar to that occurring in glasses.

Figures 7a and 8a show the temperature dependence of the bolometer signal $S(t)$ for 22 KhS ruby ceramic. Figures 7b and 8b show photographs, with the same degree of resolution, of the structure of these samples before polishing.

The character of the temperature dependence $t_M(T)$ shows that, in agreement with the theory, the arrival time of the signal peak is all the shorter the larger the grain and the lower the degree of homogeneity of the sample.

The temperature dependence $t_M(T)$ is fundamentally different, in contrast to LLZT. The arrival time of the peak value of the phonon-nonequilibrium signal increases with

decreasing temperature (phonon energy). Figure 9 shows a portion of Fig. 7b with greater magnification. One can see that the intergrain boundaries are sharp. The structure of the contact regions, however, is not resolved. For this reason, it is entirely likely that among the contact regions there are continuous regions of very small characteristic size, so that phonon transmission through such connecting necks can be determined by diffraction effects. On the other hand, quite wide but not sharp contact regions, where the fractal nature of the structure could be significant, can also be discerned. For this reason, the appearance of a dependence $S(t, T_0)$ with

$$\frac{\partial t_m}{\partial T} < 0$$

could also be associated to both effects.

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