Phononic lattices based on compacted nanoceramics

E.Salamatov,[1, a)] A.Taranov,[2] and E.Khazanov[2]

[1)]*Physical Technical Institute, UrB RAS, Izhevsk, 426000 Russia*

[2)]*Institute of Radio Engineering and Electronics, Russian Academy of Sciences, Moscow, 125009 Russia*

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It is shown, both theoretically and experimentally, that the compacted ceramics can exhibit the properties of a phononic lattice, i.e., a forbidden gap may arise in the phonon spectrum. The position and width of the gap in such systems are determined by the average grain size of ceramics, as well as by the thickness and elastic properties of the grain boundaries. In the case of composites, a dominant role in the gap formation is played by the most fine-grained phase.

I. INTRODUCTION

Nowadays considerable attention is paid to the creation of a new class of nanostructured materials in which one can control the heat flow Refs. 1–9. Since it is believed[9] that the basic element of such thermocrystals should be phononic lattices with a wide forbidden gap, it is an urgent task to find new methods for their synthesis that strike a balance between the thermo-crystal efficiency and ease of fabrication. One of the methods for obtaining phononic lattices is the compaction of ceramics from nanopowders. For the first time the possibility of existence of a forbidden gap in the phonon spectrum of compacted oxide nanoceramics was suggested in Ref. 10. This idea was then experimentally confirmed[11] in a study of the transport properties of weakly nonequilibrium phonons at helium temperatures by the phonon spectroscopy method[12] . It turned out that the anomalous growth with temperature of the phonon diffusion coefficient observed in ceramics with an average grain size less than 100 nm can be explained by the existence of such a gap. In our subsequent works, the influence of the size effects, nanoscale inclusions and pores on the position and width of the forbidden gap was studied experimentally in Refs. 13–15. All experimental results were obtained for standard samples of structural ceramics obtained by magnetic pulse compaction[16] which always exhibit a variation in grain size. The theoretical studies performed[17,18] have shown that the gap in the phonon spectrum is retained to sufficiently large values of the grain size dispersion ($\sigma \sim 0.5$), which can be realized with modern technologies of nanoceramic synthesis. Thus, there is good reason to believe that with a special sample preparation it is relatively easy to obtain

high-quality phononic crystals with a wide forbidden gap which can serve as a basis for creating thermocrystals.

In this paper we summarize the results obtained earlier and discuss the possibility of the use of compacted systems as thermocrystals.

II. EXPERIMENTAL DETERMINATION OF THE PHONON DIFFUSION COEFFICIENT IN CERAMICS AT LOW TEMPERATURES

The basic experimental method for our study of the phonon spectra is the heat pulse or phonon spectroscopy method which was proposed and developed in to study the defect structure of crystalline and amorphous solids[12,19]. The essence of the thermal phonon method is as follows. A gold film is deposited on one side of a plate made of the material under study and placed in a helium bath. The film serving as an injector of nonequilibrium phonons into the sample is heated by a short (about $10^{-7}s$) current pulse to a temperature T_h such that $\Delta T = T_h - T_0 << T_0$. This condition makes it possible to investigate the temperature dependence of phonon scattering by changing the temperature of the thermostat T_0. The opposite side of the plate is coated with a superconducting bolometer of tin or indium, the working point of which can be shifted by a magnetic field. At the temperature of the experiment inelastic phonon-phonon processes can be neglected, and the scattering efficiency is determined only by the structural features of the material and its phonon spectrum. The heat pulse method is described in more detail in Ref.[19].

The time dependence of the bolometer signal for the $ZrO_2 : Yr_2O_3$ ceramics with an average grain size of 350 nm is shown in Fig.1[11]. The inset to Fig.1 presents analogous curves for a similar sample of the same composition with the average grain size of $78nm$. In both cases, the curves are bell-shaped with a pronounced am-

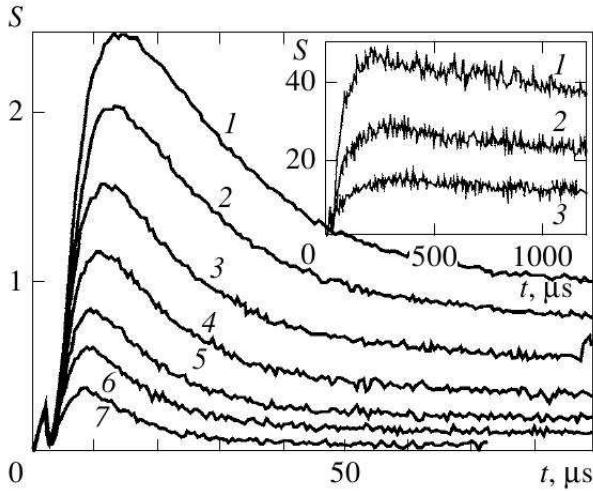[a)]Electronic mail: esalama2i@gmail.com

FIG. 1. Time dependence of the amplitude of a nonequilibrium phonon radiation signal in a sample with grain size $R_g = 359 nm$: T = 3.81 (1), 3.65 (2), 3.39 (3), 3.11 (4), 2.80 (5), 2.55 (6), and 2.28 K (7). The inset shows analogous curves for a sample with $R_g = 78 nm$: T = 3.81 (1), 3.43 (2), and 2.78 K (3) (Ref. 11).

plitude maximum at time t_{max}, which is characteristic of diffuse phonon propagation. The experiment geometry is chosen such that the flow of injected phonons obeys the one-dimensional diffusion equation

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{D}\frac{\partial T}{\partial t}, \qquad (1)$$

which allows us to express the phonon diffusion coefficient through the measured quantities t_{max} and sample thickness L: $D = L^2/2t_{max}$. A model experimental study of the phonon-impurity interaction[20] has shown that the phonon frequencies forming the maximum of the diffusion signal detected by the bolometer correspond to $\hbar\omega = (3-4)k_B T$ (k_B is the Boltzmann constant), which makes it possible to consider the phonon transport within the single-frequency model.

The most interesting result following from Fig.1 is that the temperature dependence of the diffusion coefficient ($\partial D/\partial T$) is different for ceramics with different average grain size: $\partial D/\partial T < 0$ for coarse-grained ceramics and $\partial D/\partial T > 0$ for fine-grained ones. This proves to be true for all investigated ceramics, as evidenced by Fig.2 which shows the dependence of the phonon diffusion coefficient on the average grain size of various ceramics at $T = 3.8K$. As follows from this figure, close to $R = 100nm$ a transition is observed from a linear $D(R)$ dependence for large R values to the exponential decrease in the diffusion coefficient for small ones, and it is in this range of R that the derivative $\partial D/\partial T < 0$ changes sign.

To explain this anomalous behavior of the diffusion coefficient,the phonon spectrum of ceramics and its relation to the phonon diffusion coefficient was discussed in more detail in Ref. 13, 17, and 18.
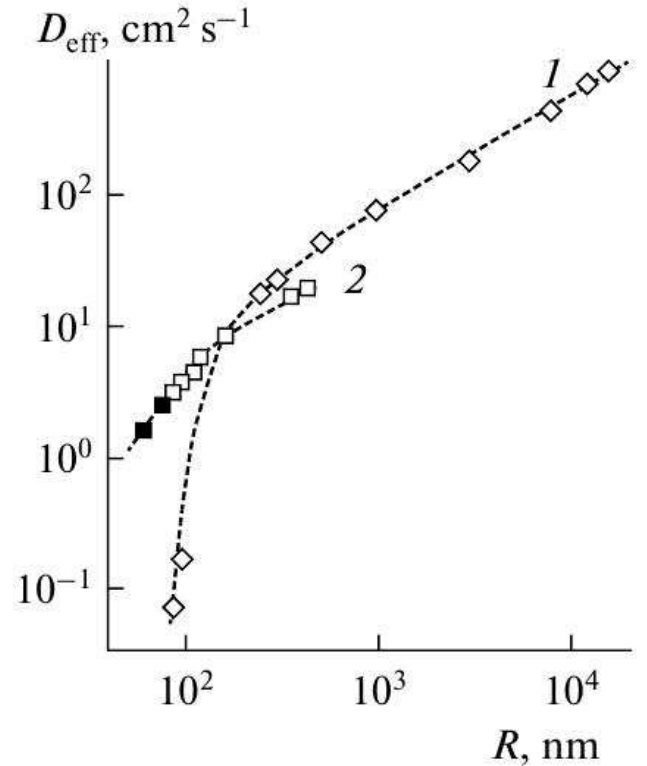

FIG. 2. The phonon diffusion coefficient as a function of the average grain size at T = 3.8 K for the Al_2O_3 (1) and YSZ (2) specimens.

III. PHONON SPECTRUM AND DIFFUSION COEFFICIENT OF CERAMIC MATERIALS

The model system in Refs. 13, 17, and 18 was considered to be an elastic medium of density ρ_0, the elastic properties of which are described by one elastic modulus K_0 (scalar model) with the dispersion law $\omega(q) = v_0 q$ ($v_0^2 = K_0/\rho_0$, q is the wave vector) for phonons of any polarization. The phonon scattering centers were randomly space distributed spherical shells with outer radius R_g, thickness d ($d/R_g \ll 1$) and elastic parameters v_1, ρ_1 ($K_1 = v_1^2\rho_1$). These shells model the grain boundaries, and the material inside and outside them the ceramic grains. In the case of multiphase ceramics the elastic parameters of the material inside the shell (v_2, ρ_2) are different from those of the material of matrix grains. The Green function of a wave propagating in a disordered medium, in the scalar model has the form

$$G(q,\omega) = \frac{1}{\omega^2 - \omega^2(q) - \Sigma(\omega,q)}, \qquad (2)$$

where $\Sigma(\omega,q)$ is the self-energy determined by the phonon elastic scattering at inhomogeneities, which in the linear with respect to the concentration of scattering centers approximation is defined by the one-center scattering matrix $t(\omega)$ $\Sigma(\omega,q) = ct(\omega)$, where c is the relative concentration of scattering centers.
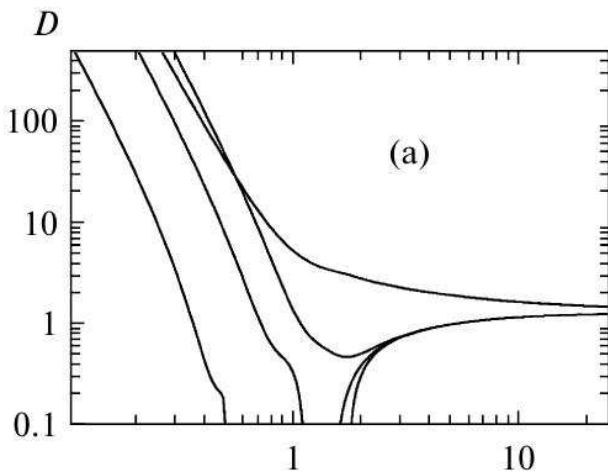
FIG. 3. The diffusion coefficient $D(x)$ calculated at $c_g = 0.5$ for different resonance frequencies: $x_r = 0.5; 1.0; 1.5$ (from bottom up). Upper curve: the case of absolutely hard spheres.

The phonon diffusion coefficient is related to the scattering matrix by the following expression[21,22]:

$$D(x, R_g) = \frac{2v_0^3}{R_g \Phi} \frac{x}{nImt(x)} = 1/3l_{tr}v_0, \qquad (3)$$

where $\Phi = \partial \ln(x^2 + cRet(x)/\partial \ln x^2$, and $x = qR_g$ is a nondimensional frequency. To determine $t(x)$, the standard problem of scattering of a plane wave by a spherical shell was solved, and it was found that when the condition $K_1/K_0 \ll 1$ is satisfied, long-wave phonons are resonantly scattered by shells at a frequency $x_r = \omega_r R_g/v_0 = \sqrt{K_1 R_g/K_0 d} < 1$. From the last inequality it follows that resonance scattering may be realized only for fine-grained ceramics, the scattering matrix being represented as

$$t(\omega^2) = \frac{3xv_0}{R_g} \frac{2x + \Gamma x^3}{x^2 - x_r^2 + \Gamma x^3} \qquad (4)$$

where Γ is the resonance width.

A detailed analysis of the phonon spectrum of disordered systems with resonance phonon scattering at defects was carried out in Ref. 22. It was shown that in this case at a sufficiently high defect concentration, cross splitting of the acoustic phonon branch is observed, and in the phonon spectrum there appears a forbidden gap, i.e. a frequency range in which phonons cannot propagate. According to[22] the bottom and top edges of the gap are defined by the expressions

$$x_{bot} \simeq x \qquad (5)$$

$$x_{top} \simeq \sqrt{x_r^2 + A(n)}, \qquad (6)$$

where x_r is the resonant scattering frequency, $A(n)$ depends on the volume fraction of scattering centers and is defined by the lattice parameter of the effective perfect

crystal. Thus, in the case of resonance scattering the phonon spectrum of such disordered systems is similar to the spectrum of a phononic crystal with a gap. The gap position is determined by the effective perfect crystal Bragg reflections, near which forbidden zones may arise, and the gap width by the concentration of spherical scattering centers (in closely packed ceramics by the average grain size). Numerical studies of the dependence of the gap position and width on the system geometry performed by the FDTD method for different materials of grains and interfaces showed the validity of the expressions obtained[17], as well as the fact that the gap in the phonon spectrum is retained to a sufficiently large spread of the grain size about the mean[18].

Correspondingly, a forbidden gap may also arise, at certain values of x_r, in the frequency spectrum of the diffusion coefficient, which is demonstrated by Fig.3. As follows from the figure, for all values of x_r in the limit of small x there occurs Rayleigh scattering ($D(x) \sim x^{-4}$), while at $x >> 1$ a purely geometric scattering ($D(x) = const$) is observed. In the range of x close to unity a change in x_r may lead to qualitative changes in the behavior of the phonon diffusion coefficient, including the

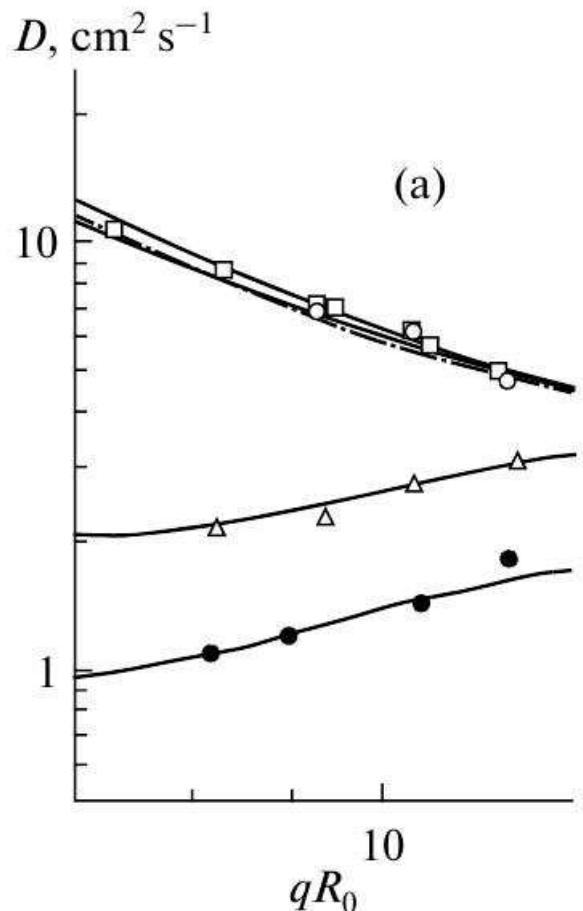FIG. 4. The phonon diffusion coefficient $D(T)$ of single-phase ceramics. From top to bottom: Rg = 135, 132, 78, 64nm.

opacity of the object to phonons (the gap formation) and a change in sign of the derivative $\partial D/\partial x$ (the presence of a minimum). It should be noted that at resonance scattering in the model there remain two independent parameters: the volume fraction of scattering centers c, and the resonance frequency

x_r that is determined by both geometric and elastic parameters of the system. In the case of dense single-phase ceramics c is practically independent of the method of sample preparation, while the resonance frequency is easy to control in the process of ceramics manufacturing, for example, by adding a plasticizer during compaction or choosing appropriate temperature regime of sintering. By way of example, Fig.4 presents the experimental points and the dependences $D(T)$ calculated in the framework of this approach in the single-frequency approximation ($\omega \sim T$) for monophase YSZ ceramics sintered under different temperature conditions and therefore differing in grain size. However, the grain size of these ceramics is not sufficiently small to cause the formation of a gap in the phonon spectrum of nanoceramics, and for ceramics with a grain size of about $60nm$ there exists only a minimum in the $D(T)$ dependence (see the inset to Fig.4). At present, it is not possible to obtain monophase ceramics with a grain size of about $10nm$ by compacting, which does not exclude the creation, on their basis, of composites which contain, along with the main fraction, a certain amount of the nanostructured phase of another material. Let us consider the effect of nanosized inclusions on the phonon spectrum of ceramics.

IV. THE ROLE OF NANOSIZED INCLUSIONS AND PORES IN THE GAP FORMATION IN THE PHONON SPECTRUM

The formation of a gap in the frequency spectrum of the diffusion coefficient when introducing into the ceramic matrix nanosized inclusions of another phase or pores, is depicted in Fig.5. The figure presents the diffusion coefficients of the two-phase ceramics obtained by the addition to a YSZ matrix of nanosized Al_2O_3 inclusions in which during sintering there occurs a phase transition resulting in the appearance of shrinkage pores. The size of grains and pores, as well as the pore concentration are determined by the temperature regime of sintering. As follows from the figure, the gap in the phonon spectrum arises at a pore size of about 10 nm.

Consider in more detail the effect of pores on the phonon spectrum of ceramics. In the approach used, the matrix of phonon scattering by spherical pores formally coincides with the resonance matrix (3) for $x_r = 0$. The gap in this case extends from zero to the top edge $x_{top,p} = \sqrt{6c_p}R_g/R_p$ (c_p, R_p are, respectively, the volume fraction of pores and their radius). A similar situation is observed in the lattice model for the case of phonon scattering by substitutional impurity atoms with an infinitely large mass[22]. The absence of acoustic vibrations in dis-

ordered systems, as distinct from the phononic lattices obtained by creating a superlattice of air cylinders in a thin plate, is due to the fact that in disordered systems a plane wave will necessarily be scattered by a defect in any direction of its propagation. In the case of phonon scattering by both shells and pores, in the approximation linear in concentration we have $t = c_g t_g + c_p t_p$. For geometric scattering ($x \gg 1$) where the factor Φ from (3) tends to unity, the diffusion coefficient satisfies the Matthiessen rule. In the range of $x \sim 1$ there arise interference corrections because Φ is also additive in concentration, and the forbidden gap extends from zero to the frequency

$$x_{top}^2 = \frac{1}{2}(x_{top,g}^2 + x_{top,p}^2 + \sqrt{(x_{top,g}^2 + x_{top,p}^2)^2 - 4x_r^2 x_{top,p}^2}). \quad (7)$$

Obviously, similar results may be obtained in the presence of other scattering centers, but contrary to the pore case, the bottom edge of the gap will be other than zero. Of prime importance here is the fact that inclusions or
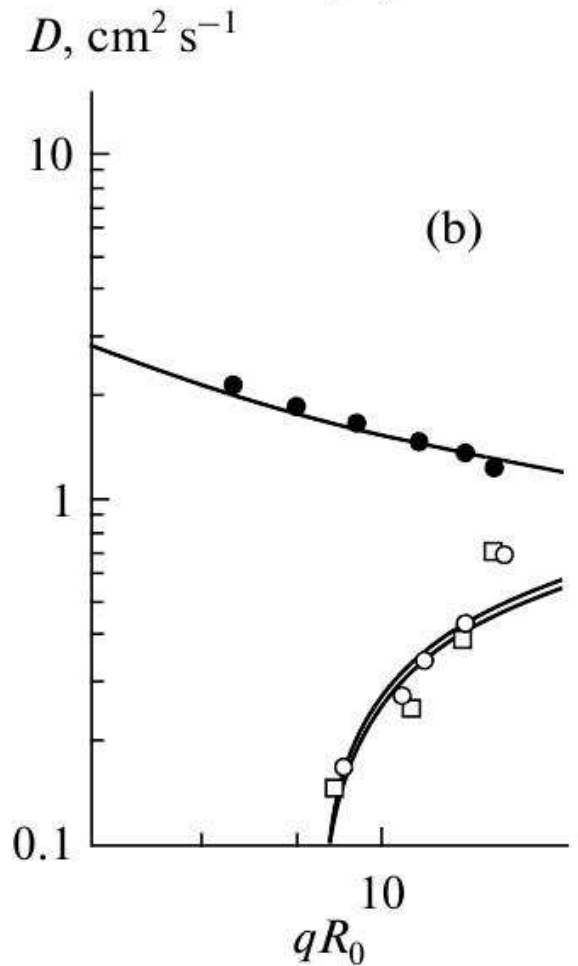

FIG. 5. The diffusion coefficient D(x) of composites with the pore size (from top to bottom) $50nm$, $15nm$, $11.5nm$.
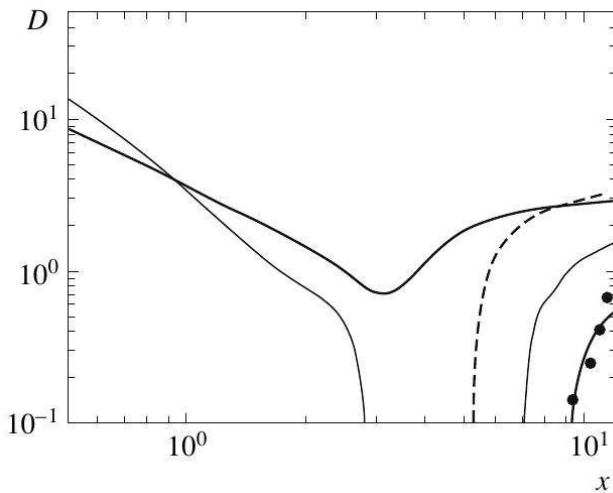
FIG. 6. The contributions to the phonon diffusion coefficient of the composite from particular defects: pores (dashed line), shells around YSZ (semibold line), and shells around Al_2O_3 grains (thin line), and the total diffusion coefficient (bold line).

pores with a characteristic size smaller than the grain size of the matrix may play a substantial role even at low concentrations, shifting the gap (or minimum) to higher frequencies.

Figure 6 illustrates the formation of a gap in the phonon spectrum of YSZ ceramics with a grain size of $70nm$, containing nanosized Al_2O_3 ($R_i = 20nm$) inclusions and sintering-induced shrinkage pores, the size of which ($R_p = 10nm$) is easily calculated. The figure shows the diffusion coefficients determined by particular defects: shells ($c_g = 0.74, c_i = c_p = 0$), pores ($c_g = c_i = 0, c_p = 0.05$), and shells around metastable inclusions of Al_2O_3 phase ($c_g = c_p = 0, c_i = 0.21$), as well as the general diffusion coefficient describing the experimental results for multiphase ceramics.

V. CONCLUSION

The paper presents the results of the studies of the phonon spectrum of ceramics obtained by compaction method, according to which the anomalous dependence of the phonon diffusion coefficient is caused by a drastic change in the phonon spectrum due to resonance phonon scattering at the ceramic grain boundaries. It is theoretically shown that in this case there occurs cross splitting of the phonon spectrum resulting in the appearance of a forbidden gap, the position and the size of which are determined by the average grain size of ceramics and the elastic properties of interfaces. In the approximation used all these parameters are related by the expression for the resonance frequency $x_r = \sqrt{K_1 R_g / K_0 d} \lesssim 1$ which implies that the gap in the phonon spectrum of ceram-

ics can arise in the case of acoustically soft grain boundaries and fine-grained ceramics with an average grain size of about $10nm$. Since monophase ceramics with such a grain size cannot be currently obtained by compaction method, the question of how the phonon spectrum may be affected by nanosized pores and inclusions of other materials is discussed. It is found that the presence of inclusions of another phase or pores with a lesser characteristic size than the grain size of the basic material (matrix), even in relatively small amounts, can lead to the appearance of a gap in the phonon spectrum and extend it to h igher frequencies.

Thus, we have experimentally shown that compacted nanoceramics can exhibit the properties of phononic lattices, namely, the presence of a forbidden gap in the phonon spectrum. The position and width of the gap is determined by geometric and elastic parameters which are readily controlled by technological expedients in the process of sample synthesis. It should be noted that all experimental results were obtained on standard samples of commercial ceramics, so one might expect that in the case of a special sample preparation (with a narrow grain size distribution, the use of plasticizers during compacting, and the choice of appropriate sintering conditions), ceramics may serve as a basis for creating phononic lattices with specified gap parameters.

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