Slow propagation of slightly nonequilibrium phonons in mixed crystals

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Anomalously slow propagation of slightly nonequilibrium phonons has been studied experimentally in several mixed crystals. The time of arrival of the signal maximum is found as a function of the temperature, length, and composition of the sample. All the results found on the propagation of slightly nonequilibrium phonons agree satisfactorily with theoretical predictions based on a model in which phonons undergo an intense Raman interaction with two-level systems in the crystal. This interaction redistributes the energy between the heat pulse and the two-level systems. The possible nature of these two-level systems in these crystals is discussed.

In mixed crystals, slightly nonequilibrium phonons injected by a warm generator are subject to strong elastic scattering, even at low temperatures $T \leqslant 4.2$ K. (A "warm" generator is one for which ΔT, the extent to which the generator temperature exceeds the reservoir temperature T, satisfies $\Delta T/T \ll 1$.) In general, the propagation of slightly nonequilibrium phonons can be described well by a diffusion equation. The time scale of the process is the arrival time of the maximum of the deviation of the phonons from equilibrium, i.e., the time $t_1 = L^2/D$, where L is the length of the sample, and D is the phonon diffusion coefficient. At temperatures $T \leqslant 4.2$ K the relaxation time of the phonon-phonon interactions, τ_f, is on the order of a few milliseconds in typical insulators, while t_1 is usually several microseconds. Consequently, if we restrict our analysis of the energy-transport processes involving slightly nonequilibrium phonons to time intervals no greater than τ_f, we can ignore the phonon-phonon interactions (Refs. 1 and 2, for example).

Under given conditions, the energy-transport process is vastly slower in glasses, polycrystalline materials, and ceramics. The response of a bolometer goes through a maximum and then slowly decreases, over a matter of milliseconds. In glasses, these "slow" transport processes result from a strong interaction with the two-level systems. In materials which are inhomogeneous at the microscopic scale (polycrystalline sample and ceramics), they are associated with a transport across grain boundaries.

In single crystals, transport processes may be slowed down because of a scattering by structural defects which is more intense than elastic scattering. An example is the "capture" of resonant phonons when a suitable system of levels (e.g., paramagnetic) is present. In the case at hand, however, this interaction is important for only a fairly narrow group of resonant phonons, which could not carry a significant fraction of the energy of the heat pulse, with its broad spectral composition.

Also of interest in connection with the slowing of transport processes are results of research on the propagation of slightly nonequilibrium phonons in yttrium-erbium-aluminum garnet (Er:YAG) single crystals.[3] Experimentally, one observes the ordinary diffusion maximum of the signal, which is precisely the same as the corresponding maxima in other yttrium-(rare earth)-aluminum garnets (RE:YAG) at low temperatures (or at a low concentration of erbium ions). In addition, one observes a second maximum, delayed with respect to the first by orders of magnitude. The typical time at which this maximum arrives, t_2, reaches hundreds of microseconds. A significant fraction (sometimes the great preponderance) of the energy of the heat pulse is associated with specifically those processes which determine the appearance of this maximum.

Under the conditions of the experiments which we are reporting here, the inequality $t_2 \ll \tau_f$ holds, so phonon-phonon interactions can be ignored. States associated with the paramagnetic properties of Er^{3+} ion in a garnet lattice have been studied thoroughly. Such states could not have any important effect on phonon scattering. We recall that the first excited state of the Er^{3+} ion in the YAG lattice has an energy of 24 cm^{-1}. At $T \leqslant 4.2$ K, this state could not be responsible for the observed features in the propagation of slightly nonequilibrium phonons, according to estimates.

Experimental results obtained in Ref. 3 are evidence in favor of energy states with a splitting on the order of 5 K in the Er:YAG crystal. These states are undoubtedly associated with specifically the Er dopant, since these states are not seen in experiments on the propagation of slightly nonequilibrium phonons in other mixed RE:YAG mixed crystals (except YAG:Ho). This new state could hardly be paramagnetic, since the system of paramagnetic levels of Er^{3+} in the garnet lattice is well known, and this state is not there. Furthermore, the spin-lattice coupling constant is low for paramagnetic levels, and it could be responsible for the strong coupling and, correspondingly, the strong scattering for only the group of resonant phonons.

Incorporating a possible broadening of the levels of paramagnetic origin due to a dipole-dipole interaction could not lead to any important effects. In the first place, the fraction of the energy of the heat pulse which is carried by the phonons of this group is too small to explain the observed features. Finally, direct experimental results on the propagation of slightly nonequilibrium phonons in RE:YAG solid solutions $Y_{3-x}R_xAl_5O_{12}$, in which the paramagnetic R^{3+} ions do have a suitable system of levels (for Tb, $\Delta = 5$ cm^{-1}), agree with the corresponding results on the diamagnetic system $Y_{3-x}Lu_xAl_5O_{12}$. In other words, these results demonstrate the appearance of only an elastic scattering, which—for identical concentrations of the rare earth and for random distributions of the yttrium and R ions among lat-

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tice sites—should be essentially identical for all the rare earths from Gd to Lu.

The question of the reasons for the slowing of energy transport in mixed $Y_{3-x}Er_xAl_5O_{12}$ crystals and the question of the nature of the observed excitations (which we will attribute below to the existence of two-level systems) remain open. Answering these questions requires a detailed theoretical and experimental study of slow transport processes involving slightly nonequilibrium phonons in mixed crystals. Such a study was the goal of the work which we are reporting here.

A slow transport of slightly nonequilibrium phonons is not peculiar to the $Y_{3-x}Er_xAl_5O_{12}$ system. Such processes are observed in a long list of mixed crystals. They can be described by a model in which the phonon transport processes are dominated by two-level systems with a spin-lattice coupling constant larger than in the case of paramagnetic levels.[4]

Let us assume, in accordance with Ref. 4, that the mixed crystal contains two-level systems with an energy gap Δ on the order of several kelvins and has a strain-energy constant on the order of a few electron volts. In this case, a fairly strong Raman scattering of phonons arises in the crystal, with a corresponding pumping of the two-level centers. We also assume that the concentration of these two-level centers or systems, N_{2LS}, is high enough that their contribution to the heat capacity is greater than the lattice contribution at the typical experimental temperatures, $2.2\ K < T < 3.8\ K$. The concentration of two-level systems can be much lower than the concentration of the less abundant component of the mixed crystal. For the mixed crystals of interest here, the corresponding condition is $10^{18}\ cm^{-3} < N_{2LS} < 10^{21}\ cm^{-3}$. According to this model, the slowing of a transport process stems from a redistribution of the energy of the generated pulse between vibrational states of the lattice and excitations of the two-level systems.

We turn now to a discussion of the experimental results. The experimental layout is standard and is described in Ref. 3. We studied the solid solution $Y_{3-x}Er_xAl_5O_{12}$ in greatest detail. Figure 1 shows typical curves of the temperature dependence of the arrival time of the maximum of the deviation of the phonons from equilibrium, $t_2(T)$, in the slow process for samples of various compositions and various lengths (from 0.065 to 1.3 cm). The ratio of the linear dimension of the generator, l_H, to the length of the sample was chosen to be the same in all cases, so that geometric factors can be ignored in the analysis of the results. The series of curves from a) to d) in Fig. 1 corresponds to increasing Er concentration in the garnet solid solution. Each of the series corresponds to a set of samples of various lengths; the length decreases with decreasing curve label. It follows from the series of curves in Fig. 1 that the characteristic manifestations of slow processes (large absolute values of t_2 and a change in the sign of the slope of the temperature dependence, from positive to negative) become more prominent as the Er concentration and the length of the sample increase. Particularly noteworthy is the experimental change in the sign of the derivative $dt_2(T)/dT$ for a series of samples having the same composition but differing in length (Fig. 1c).

The general picture of the transformation of the $t_2(T)$ curves in Fig. 1 is described completely by the theory at a qualitative level.

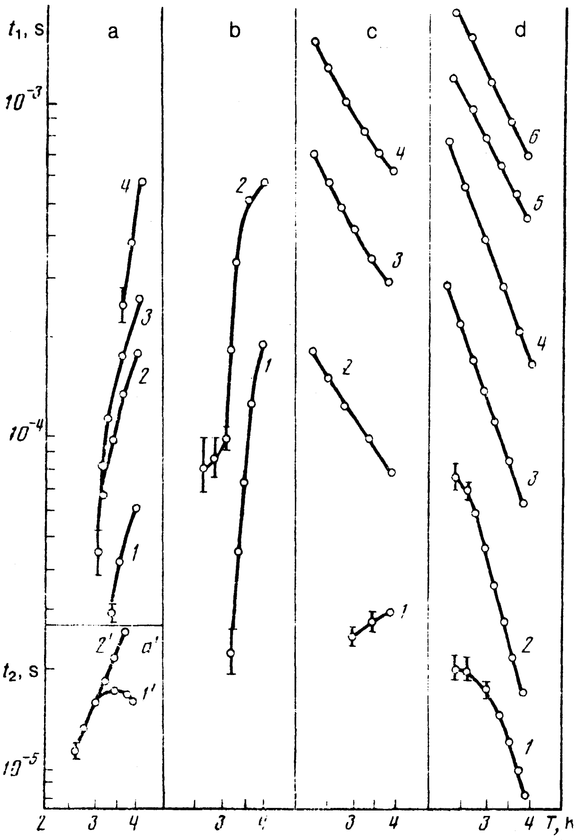

FIG. 1. Signals representing the deviation from a phonon equilibrium detected by a bolometer in samples of $Y_{3-x}Er_xAl_5O_{12}$. a—$x = 0.2$, $L = 0.4$ (1), 0.68 (2), 0.95 cm (3); $Ga_{2.8}Er_{0.2}Cd_5O_{12}$ sample, $L = 0.4$ cm (4); a′—arrival time of the first diffusion maximum on the signal of the deviation from phonon equilibrium in samples of $Y_{2.8}Er_{0.2}Al_5O_{12}$, $L = 0.68$ cm (1′), $Y_{2.8}Lu_{0.2}Al_5O_{12}$, $L = 0.68$ cm (2′); b—$x = 0.6$, $L = 0.4$ (1), 0.68 cm (2); c—$x = 1$, $L = 0.065$ (1), 0.12 (2), 0.25 (3), 0.5 cm (4); d—$x = 3$, $L = 0.018$ (1), 0.03 (2), 0.07 (3), 0.14 (4), 0.22 (5) cm; sample of $Ho_3Al_5O_{12}$, $L = 0.03$ cm (6). The power dissipation at the heater was $P_H < 0.1\ W/mm^2$, $l_H/L \approx 2$.

We have yet a few more words about the curves in Fig. 1. Figure 1d shows $t_2(T)$ for a $Ho_3Al_5O_{12}$ sample. This curve is qualitatively the same as the curve for $Er_3Al_5O_{12}$. For samples of the same length, the value of t_2 turns out to be far larger. The slow processes are more prominent in Ho:YAG.

Finally, Fig. 1a shows, for comparison, curves of the arrival time of the maximum of the deviation of the phonons from equilibrium, $t_1(T)$, due to diffusion in the mixed crystal in the case of a strong elastic scattering (Rayleigh scattering) by structural defects, versus the temperature. This figure demonstrates the order-of-magnitude difference between the values of $t_1(T)$ and $t_2(T)$. We will be discussing this result in more detail below.

According to Ref. 4, the parameter which basically determines the nature of the $t_2(T)$ curve is the quantity $B = [l_R(\omega_d)/L]^2$, where l_R is the distance traveled by a phonon over the Raman-interaction time τ_R, and ω_d is the frequency of the predominant group of phonons, i.e., the group contributing most in the transport process. In general, the frequency ω_d is a function of the variables T and L. For this reason, we will have to work with measurements of $t_2(T)$ for samples of identical length in order to correctly compare theoretical and experimental results and to evalu-

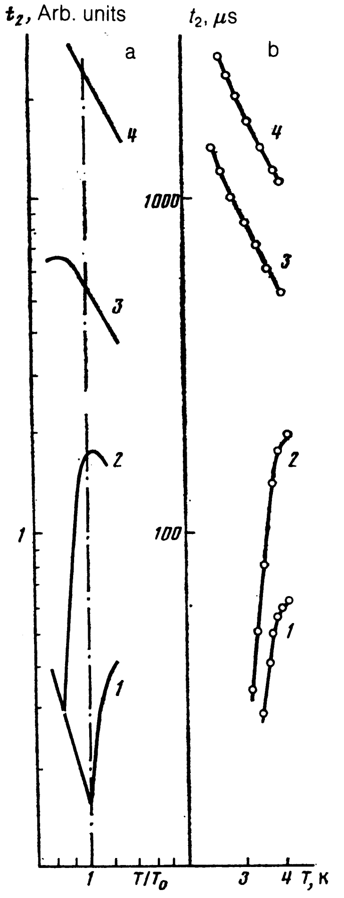

FIG. 2. a: Calculated temperature dependence of the arrival time of the signal maximum in the slow process. 1—$B = 1.5$; 2—0.17; 3—0.06; 4—0.007. b: Measured temperature dependence $t_2(T)$ for $Y_{3-x} \cdot Er_xAl_5O_{12}$ samples of identical length $L = 0.4$ cm. 1—$x = 0.2$ ($B = 1.5$); 2—$x = 0.6$ ($B = 0.17$); 3—$x = 1$ ($B = 0.06$); 4—$x = 3$ ($B = 0.007$).

ate the role played by Raman pumping.

Figure 2 shows results calculated on the dependence $t_2(T)$ for several values of the parameter B, divided by the average temperature of the measurement interval (T_0). Also shown here are experimental data for samples of the same length but different compositions. The reason for the differences in the value of B under these experimental conditions is that l_R varies because of a change in the concentration of the two-level systems. The reason why we selected from the various theoretical curves those corresponding to the parameter values $B = 1.5$, 0.17, 0.06, and 0.007 is that these values of B correspond to the experimental conditions, according to independent estimates (more on this below).

To determine how well the theoretical and experimental results in Fig. 2, a and b, agree, let us determine the order of magnitude of this parameter from independent experiments. Figure 3 shows the time evolution of the bolometer signal in $Y_{2.8}Er_{0.2}Al_5O_{12}$ and $Y_{2.8}Lu_{0.2}Al_5O_{12}$ samples of identical length for several crystal temperatures. In the $Y_{2.8}Lu_{0.2}Al_5O_{12}$ sample, the signal maximum is determined exclusively by the Rayleigh scattering of the slightly nonequilibrium phonons. One might suggest that the intensity of elastic scattering $Y_{2.8}Er_{0.2}Al_5O_{12}$ is essentially the same as that in $Y_{2.8}Lu_{0.2}Al_5O_{12}$, because of the approximately equal masses of Er and Lu and also because the force constants of the lattice are essentially unchanged from those of the ideal crystal matrix by the isomorphic substitution Y↔Er.

At $T < 2.9$ K, the slow transport processes associated with the presence of Er are not seen, and the curves for the two crystals coincide (curves 3 in Fig. 3). This result means that at this temperature in the $Y_{2.8}Er_{0.2}Al_5O_{12}$ sample we have $l_R(\omega_d) \simeq (D\tau_R)^{1/2} > L$. We can thus estimate the order of magnitude of l_R and τ_R for the given temperature and for the given concentration of the rare-earth dopant. The value of D can be found from the arrival time of the signal maximum in the $Y_{2.8}Lu_{0.2}Al_5O_{12}$ sample. For the $Y_{2.8}Er_{0.2}Al_5O_{12}$ sample at $T = 2.9$ K we thus have $l_R > L = 0.68$ cm and $\tau_R \geqslant 1.5 \cdot 10^{-5}$ s. Assuming $\tau_R \sim 1/N_{2LS}$ and $N_{2LS} \sim x$, we can also find rough estimates of B at $T = 2.9$ K for the samples with other Er concentrations, at a fixed thickness. The results of these estimates are shown in Fig. 2b, where each measured $t_2(T)$ curve corresponds to the values of $B(T_0 = 2.9\text{ K})$ determined in this manner. A comparison of this parametric family of curves with the theoretical curves for approximately the same values of the parameter B reveals a satisfactory agreement between theory and experiment.

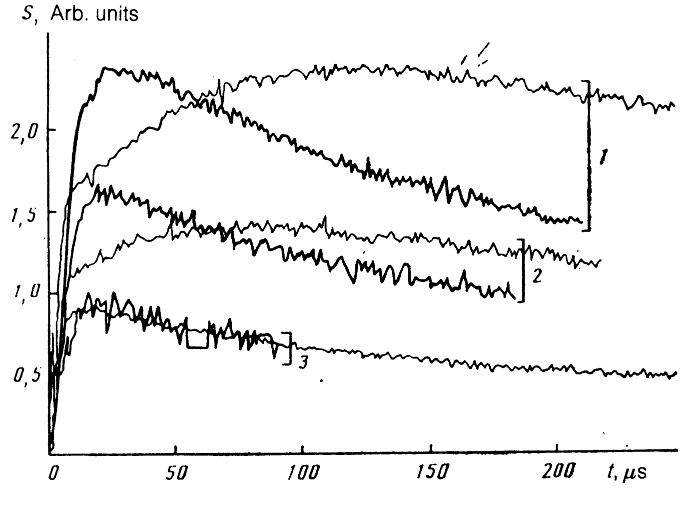

FIG. 3. Signals representing the deviation from a phonon equilibirum detected by a bolometer in samples of $Y_{2.8}Er_{0.2} \cdot Al_5O_{12}$ and $Y_{2.8}Lu_{0.2}Al_5O_{12}$ (the brighter line) with $L = 0.68$ cm for various sample temperatures: 1—$T = 3.83$, 2—3.43; 3—2.91 K. $P_H = 10^{-2}$ W/mm², $l_H/L = 1$.

An essentially similar estimate of l_R and τ_R can be found by comparing the $t_1(T)$ curves in the inset in Fig. 1a for $Y_{2.8}Lu_{0.2}Al_5O_{12}$ and $Y_{2.8}Er_{0.2}Al_5O_{12}$. At $T = 2.9$ K we have $t_1 \simeq 1.5 \cdot 10^{-5}$ s for both solid solutions. At higher temperatures, the behavior of the arrival time of the first maximum of the phonon deviation from equilibrium in Er:YAG is quite different from the $t_1(T) \sim T^4$ law characteristic of a Rayleigh scattering of phonons by point defects. The theoretical expression describing the first maximum of the signal representing the deviation from a phonon equilibrium, $S_1(t)$, in $Y_{3-x}Er_xAl_5O_{12}$ is

$$S_1(t) \dot{\sim} \int_0 d\omega \rho(\omega) \hbar\omega n(\omega) \frac{1}{2(\pi D(\omega) t)^{1/2}} \times \exp\left\{-\frac{L^2}{4D(\omega)t} - \frac{t}{\tau_R(\omega)}\right\}. \qquad (1)$$

Here $\rho(\omega)$ is the phonon density of states, $\hbar\omega$ is the energy, and $n(\omega)$ is a Planckian distribution function of the phonons. This expression was derived for one-dimensional diffusion. It is also a simplified expression, since it incorporates only the decrease in the number of particles in the diffusion flux due to the Raman pumping of the two-level centers. The influx of phonons into the long-wavelength part of the spectrum during Raman scattering of high-frequency phonons accompanied by the excitation of the center is completely ignored. In other words, the contribution of phonons with an energy $\hbar\omega - \Delta$, which arise in collisions of phonons with an energy $\hbar\omega$ with unexcited centers, is ignored. We will return to the role played by these phonons. If the temperature is low enough, we have $e^{-t/\tau_R} \simeq 1$ for the fundamental group of phonons, and the signals in $Y_{2.8}Er_{0.2}Al_5O_{12}$ and $Y_{2.8}Lu_{0.2}Al_5O_{12}$ are the same. For our experimental conditions, this temperature region is $T < 2.9$ K.

As the temperature is raised, the quantity $t_I(T) = L^2/2D(T)$ increases, and it becomes greater than $\tau_R(T)$. Setting

$$t_1(\omega) = t_1(T)\,(\hbar\omega/k_B T)^4$$

and (for simplicity)

$$\tau_R(\omega) \sim \tau_R(T)\,(\omega/T)^{-4}$$

we find an exponential factor

$$\exp\{-[(t_1/t + t/\tau_R)\,(\hbar\omega/k_B T)^4]\}.$$

in (1). The minimum value of the quantity $t_I/t + t/\tau_R$ is reached at $t_0 = (t_I \tau_R)^{1/2}$. The signal maximum is evidently reached at the same time. We can use

$$S_1(t) \sim \frac{1}{(t_1/t + t/\tau_R)^{5/4}}$$

as a rough estimate. It is easy to see that t_0 does not depend on the temperature and is proportional to L. We thus see that the inequality $t_1 \sim T^4 L^2$ can indeed serve as the condition under which the arrival time of the first maximum of the deviation from phonon equilibrium does not conform to the $t_1(T) \gg \tau_R(T)$ law.

A basic assumption of the theory of Ref. 4 is that when Raman scattering is sufficiently strong most of the heat-pulse energy accumulates in the system of two-level centers over a time $t \gg \tau_R(T)$. The transfer of excitation from center to center occurs either in the course of a spin-lattice relaxation of the centers, possibly followed by Raman scattering, or in the course of the emission and reabsorption of resonant phonons, with spectral diffusion.[5-7] The approximation used here seems to be fairly good in the case of a strong Raman interaction, in which repeated Raman-scattering events are important. This situation promotes the accumulation of the preponderance of the heat-pulse energy in the system of centers. In other words, the theory must give a more accurate description of the experimental results at sufficiently small values of the parameter B (in Fig. 1, this situation corresponds to the successive transition from Fig. 1a to Fig. 1d, and from the lower curves to the upper ones within each frame of this figure).

It is furthermore obvious that the contribution to the signal from the phonons which carry off an energy $\hbar\omega - \Delta$ after the excitation of a center (and also the contribution of the nonresonant phonons formed as a result of spin-lattice relaxation) should increase at lower experimental temperatures, because of the weakening of the Raman pumping.

In Ref. 4, where an iterative procedure was proposed for finding a solution for the nonequilibrium increments in the distribution function of the nonequilibrium phonons and spins, an expression for the temperature dependence of the second signal maximum, $S_2(T)$, was derived through the use of the zeroth-order iteration. In other words, the phonon contribution which we just mentioned was ignored. In this connection, if the parameter B is not too small the detailed shape of the signal representing the deviation from phonon equilibrium should differ from the calculated shape, and it should provide additional information about slow transport processes.

The discrepancy with theory should be greatest for the samples corresponding to the lower curves in Figs. 1b and 1c and also to curves of the type in Fig. 1a, if it were found possible to carry out measurements on short samples. These are the samples which have the largest values of B among all the samples available.

Let us discuss this point in more detail. Figure 4, a and b, shows the signal $S(t)$ in $Y_2Er_1Al_5O_{12}$ samples; part a corresponds to $L = 0.14$ cm, and part b to $L = 0.065$ cm. Figure 5 shows the corresponding results for a $Y_{2.4}Er_{0.6}Al_5O_{12}$ sample with $L = 0.68$ cm. This set of curves corresponds to very nearly the same value of the parameter B at which the transformation of the curves occurs as the sign of the derivative dt_2/dt changes. A noteworthy feature of the curves in Fig. 4, a and b, and Fig. 5 is the appearance of a third maximum in the signal, which takes an intermediate position between the two maxima described above. Its position, like the position of the main maximum, which is determined by a slow energy-transport process, is shown by the arrows.

The behavior of this additional maximum suggests that it, too, is due to slow processes. Specifically, according to the arguments above for higher experimental temperatures (the upper curves in Figs. 4 a and b, and Fig. 5), this maximum is not seen for either the $Y_2Er_1Al_5O_{12}$ sample or the $Y_{2.4}Er_{0.6}Al_5O_{12}$ sample. At the same experimental temperatures, this maximum is seen considerably more clearly in the shorter $Y_2Er_1Al_5O_{12}$ sample (Fig. 4b) than in the sample of the same composition in Fig. 4a. This result could also have

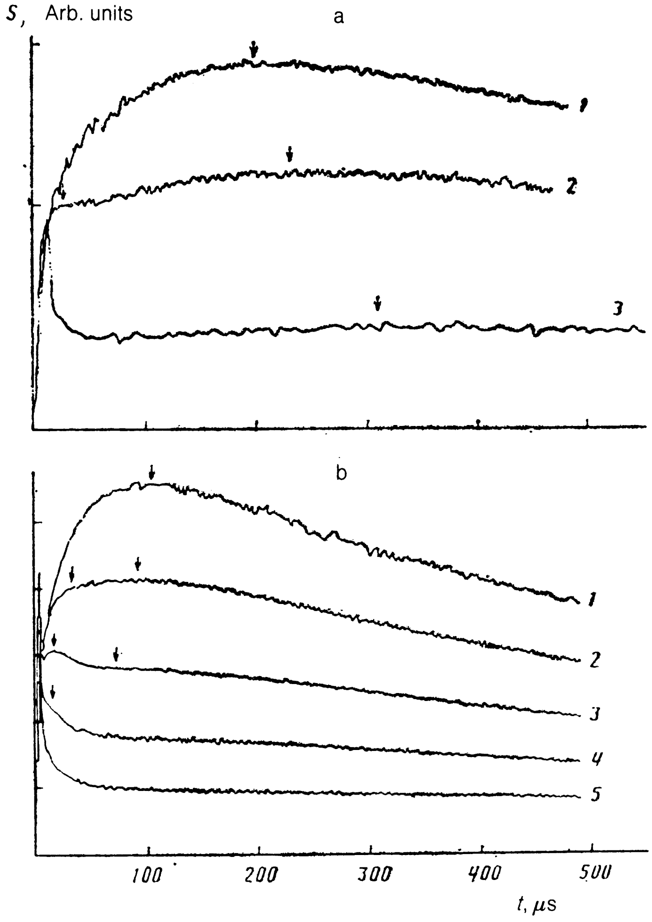

FIG. 4. Signals representing the deviation from a phonon equilibirum detected by a bolometer in a sample of $Y_2Er_1Al_5O_{12}$. a: $L = 0.14$ cm. 1—$T = 3.44$; 2—3.08; 3—2.71 K. b: $L = 0.065$ cm. 1—$T = 3.83$; 2—3.5; 3—3.21; 4—2.99; 5—2.69 K. $P_H = 0.1$ W/mm^2.

been predicted, since the parameter B increases as we go from a sample with a length $L = 0.14$ cm to one with $L = 0.065$ cm.

An important characteristic of this additional maximum is the very strong temperature dependence of its position, which is similar to the curve in Fig. 1a. This result again can be understood on the basis of the model which we are using here. Specifically, if we put aside the point that the generation of phonons with frequencies $\hbar\omega - \Delta$ occurs continuously in the course of the Raman interaction, we can think of the contribution of these phonons to the signal as resulting from an injection into the crystal of a new heat pulse after a time $\sim \tau_R$. The spectrum of this pulse, however, corresponds to a lower generator temperature. In this case the effective value of the parameter B for these phonons is larger than that for the phonons of the original heat pulse.

In agreement with our general results, this conclusion (first) means a shift of the new maximum to a shorter arrival time (for the same sample length) and (second) explains the strong temperature dependence of the position of this maximum, with a positive derivative. This point is demonstrated clearly by the set of curves in Fig. 2, a and b. The upper curves transform into the lower curves with increasing value of the parameter B. Accordingly, even under conditions such that the original parameter B corresponds to an intermediate value, which leads to a negative value of the derivative dt_2/dT (see Fig. 4b and also the second curve from the bottom in Fig. 1c), the derivative dt_2/dT is positive for the additional maximum, and the dependence itself is strong.

Completing our discussion of slow processes by which slightly nonequilibrium phonons propagate through the mixed $Y_{3-x}Er_xAl_5O_{12}$ crystal, we show how the arrival time of the signal maximum depends on the composition of the crystal (Fig. 6). The lower curve here corresponds to the position of the ordinary diffusion maximum, $t_1(x)$, in $Y_{3-x}R_xAl_5O_{12}$ crystals. The same curve should describe the dependence $t_1(x)$ in $Y_{3-x}Er_xAl_5O_{12}$ crystals in the absence of a Raman pumping of two-level centers. The upper curve describes the $t_2(x)$ dependence for $Y_{3-x}Er_xAl_5O_{12}$. As expected, the transport process slows down with increasing x. This behavior corresponds to the simple suggestion that with increasing Er concentration in the mixed crystal there is a corresponding increase in the number of two-level centers. As a result, there is a decrease in l_R and in the parameter B. Shown for comparison in this figure are corresponding curves for slow transport in $Y_{3-x}Ho_xAl_5O_{12}$ and in a mixed crystal consisting of alumomagnesium spinel with manganese, $MgAl_{2-x}Mn_xO_4$. These curves are similar to that observed in the $Y_{3-x}Er_xAl_5O_{12}$ crystal, but the signal delay is most obvious here.

A long signal delay is observed in mixed crystals of calcium fluorite with erbium. Some typical curves are shown in Fig. 7. Shown in the inset here is a curve corresponding to a pure calcium fluorite crystal. This curve describes a ballistic propagation of phonons. Curves 1–4 correspond to the propagation of slightly nonequilibrium phonons in Er:CaF_2 mixed crystals with a 20% Er content instead of Ca. These curves describe a slow transport process, with a typical temperature dependence of the arrival time of the signal maximum, $t_2(T)$, as in Fig. 1, c and d. It was shown experimentally in Ref. 8 that two-level centers exist in structures of the fluorite type $(CaF_2)_{1-x}(RF_3)_x$. They result from a tunneling of a noncentral F^- ion in R_6F_{37} clusters. Under the assumption that the density of states remains constant to 100 cm^{-1}, we find its value to be $n \simeq 10^{33}$ erg$^{-1}\cdot$cm^{-3}. This value corresponds to the presence of 10^{19} cm^{-3} two-level centers. The slow propagation of slightly nonequilibrium phonons which we have observed probably stems from the presence of these two-level systems. We will not go into this case in more detail here, since our model does not assume a wide spectral distribution of two-level systems, as occurs in glasses. The temperature dependence of the arrival time of the signal maximum observed in glasses is extremely sharp and is characterized by a positive derivative. The $t_2(T)$ dependence which we observed in $(CaF_2)_{1-x}(ErF_3)_x$ with $dT_2/dT < 0$ probably means that Raman scattering of phonons is playing an important role in this case.

We have also observed slow propagation of slightly nonequilibrium phonons in the mixed crystals calcium-niobium-gallium garnet (CNGG) (Fig. 8a) and yttrium aluminate, $Y_{1-x}Er_xAlO_3$ (Fig. 8b). Shown in these figures are curves of the temperature dependence of the arrival time of the signal maximum, normalized to the square of the sample thickness. At low temperatures the dependence becomes

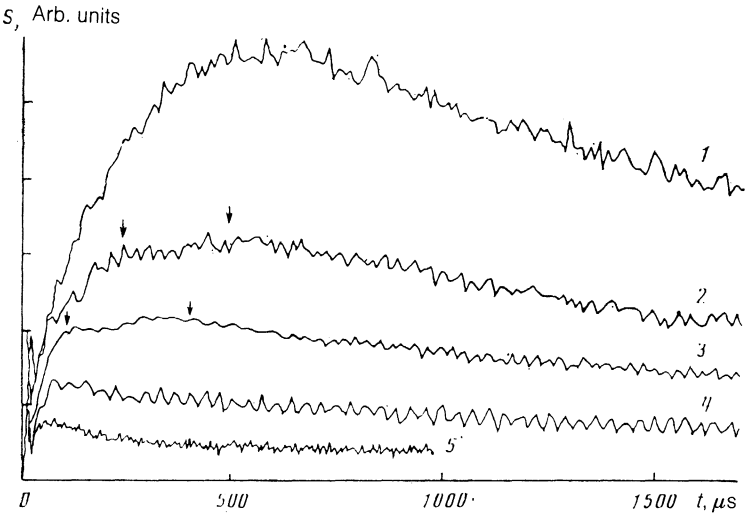

FIG. 5. Signals representing the deviation from a phonon equilibrium detected by a bolometer in a sample of $Y_{2.4}Er_{0.6}Al_5O_{12}$: $L = 0.68$ cm. 1—$T = 3.78$; 2—3.41; 3—3.18; 4—2.99; 5—2.73 K.

strong. The delay of the signal reaches 100 μs for samples 1 cm thick. Very simple estimates of the intensity of the elastic scattering of phonons in CNGG and Nd:CNGG show that the Rayleigh scattering is less apparent than in the mixed RE:YAG crystals. Consequently, the measured arrival times of the signal maximum, $t_M(T)$, are significantly greater than the times determined by elastic scattering. They probably correspond to a slow transport process. Experimental data on the propagation of slightly nonequilibrium phonons in CNGG and Nd:CNGG crystals can then be explained in a natural way on the basis of the model of slow transport processes proposed here. The curves in Fig. 8 are similar to the curves in Fig. 1, a and b, with relatively large values of the parameter B. In the shortest sample, with $L = 0.26$ cm, the reason for the weaker temperature dependence $t(T)$ may be a weakening of the role of Raman pumping. The curves in Fig. 8b for the mixed yttrium-erbium aluminate crystals are similar. They also exhibit a strong temperature dependence $t(T)$ at low temperatures. Experiments have been carried out for samples of various compositions, however, and in this case the energy transport seems to be determined by a slow process. The lower curve in Fig. 8b corresponds to the $YAlO_3$ matrix crystal. This curve demonstrates that the crystalline matrix has a strong elastic scattering of the Rayleigh type, which is probably a consequence of structural defects.

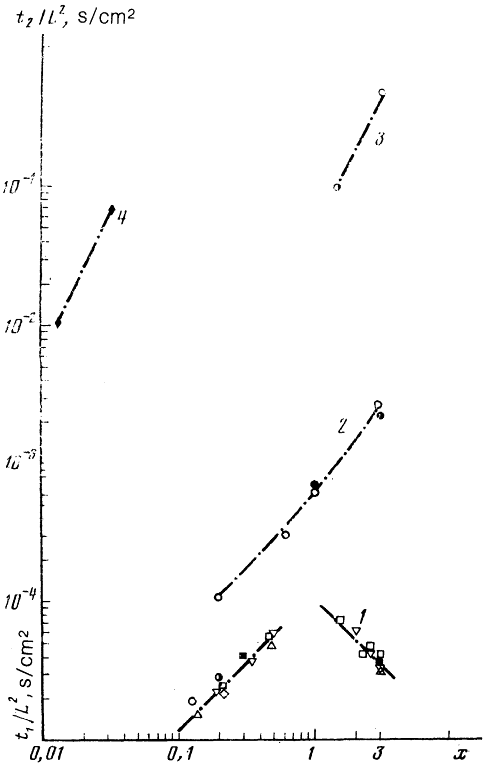

FIG. 6. Concentration dependence of the arrival time of the signal maximum, normalized to the square of the length, in samples of $Y_{3-x}R_xAl_5O_{12}$ [R = Lu(∇), Yb (Δ), Tm (■), Er (○), Ho (▲), Dy (□), Tb (◊)] and $Y_{3-x}Er_xAl_{1.95}Sc_{0.05}(AlO_4)_3$ (●) and Mn:$MgAl_2O_4$ (◆), $T_H = 3.4$ K, $P_H = 10^{-2}$ W/mm². 1—Normalized arrival time of the signal maximum when only the elastic scattering due to the random distribution of masses in the mixed garnet crystals with an isomorphic substitution Y↔R is taken into account; 2–4—normalized arrival time of the signal maximum in: 2—$Y_{3-x}Er_xAl_5O_{12}$; 3—$Y_{3-x}Ho_xAl_5O_{12}$; 4—$MgAl_{2-x}Mn_xO_4$.

In the CNGG and $Y_{1-x}Er_xAlO_3$ crystals, we were not able to see the usual first maximum, due to a diffusion of long-wavelength phonons. A possible explanation is the presence of two-level systems with an energy gap Δ smaller than in $Y_{3-x}Er_xAl_5O_{12}$ crystals, in which case this maximum is clearly observed in samples with a relatively large value of the parameter B (Fig. 1a).

An interesting modification of the slow transport process from that in the CNGG crystal is found in Er:CNGG. Figure 9 shows the shape of the signal for two CNGG and Er:CNGG crystals with identical thicknesses at a fixed temperature. We clearly see the appearance of an additional, broad maximum in the signal. This maximum causes a substantial transformation of the entire propagation curve of the slightly nonequilibrium phonons. It suppresses the maximum due to two-level systems in CNGG. It is undoubtedly associated with a role of erbium ions in forming new two-level systems in the garnet structure.

Let us look at some numerical estimates for $Y_{3-x}Er_xAl_5O_{12}$. The expression for $1/\tau_R$ [expression (7) in Ref. 4] for $\hbar\omega > \Delta$ and $k_B T \simeq \Delta$ can be approximated by

$$\frac{1}{\tau_R} = \frac{\pi}{2}(N_{2LS}a_0^3)a_0^3\left(\frac{\Lambda}{Mv_S^2}\right)^2 \hbar\omega^2\rho(\omega),$$

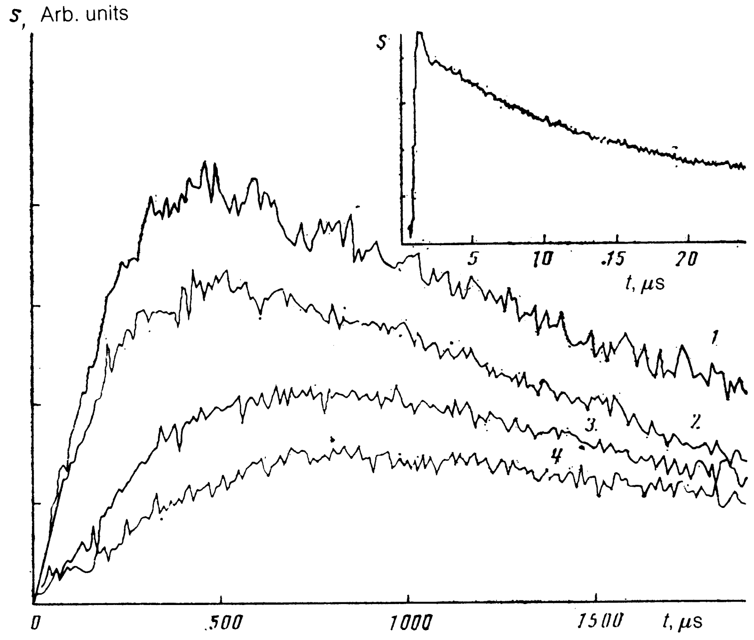

FIG. 7. Signals representing the deviation from a phonon equilibrium which are detected by the bolometer in a sample of CaF_2 (20% Er); $L = 0.028$ cm, $T = 3.69$ (1), 3.35 (2), 2.99 (3), 2.37 (4) K; $P_H = 0.2$ W/mm^2. The inset shows the signal in (0.3% EuF_3):CaF_2; $L = 0.3$ cm, $P_H < 0.1$ W/mm^2.

where a_0^3 is the volume of the unit cell, Λ is the strain-energy constant for a two-level center, M is its mass, and v_s is the velocity of sound. As the frequency of the predominant phonons we adopt $\omega_d \simeq (3k_B T)/\hbar$, which corresponds to the maximum of the energy density in the heat pulse at a generator temperature T. For $T = 2.9$ K we would have $\omega_d \simeq 1.2 \times 10^{12}\,s^{-1}$. We assume $x = 0.2$, $\tau_R = 1.5 \cdot 10^{-5}$ s, and $N_{2LS} \simeq 5 \cdot 10^{18}$ cm^{-3}. Substituting in the values $a_0 \simeq 10^{-7}$ cm and $v_s \simeq 5.6 \cdot 10^5$ cm/s, we find $\Lambda \simeq 0.07 M V_s$. If we use the mass of Er as the mass of the two-level center, we find $\Lambda \simeq 4.3$ eV, while if we use the mass of oxygen as M we find $\Lambda = 0.4$ eV.

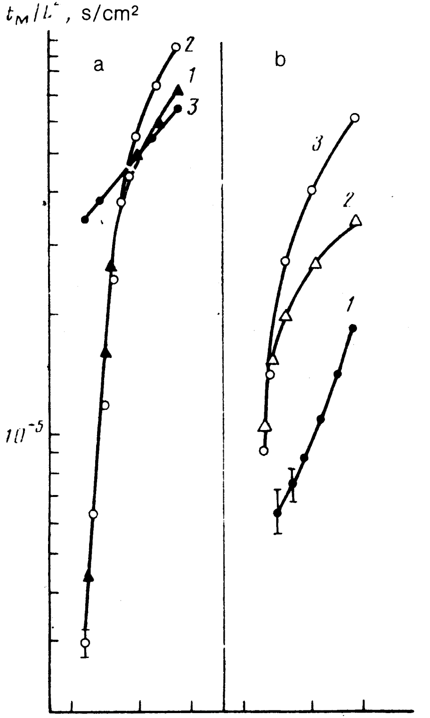

FIG. 8. Arrival time of the signal maximum, normalized to the square of the length, versus the temperature. a: In samples of cation–vacancy garnets. 1—$Ca_3Nb_{1.69}Ga_{3.2}N_{0.11}O_{12}$ (CNGG), $L = 0.92$ cm, $P_H < 0.1$ W/mm^2, 2,3—(1% Nd):CNGG, $L = 1.3$ and 0.26 cm, respectively, $P_H < 0.1$ W/mm^2. b: In samples of $Y_{1-x}Er_xAlO_3$. 1—$x = 0$, $L = 0.9$ cm; 2—$x = 0.07$, $L = 0.77$ cm; 3—$x = 0.2$, $L = 0.76$ cm; $P_H < 0.1$ W/mm^2.

Analyzing the entire set of experimental data on slow propagation processes of slightly nonequilibrium phonons in mixed crystals, we can offer the following suggestion regarding the nature of the two-level centers.

In all the crystals which were used, except calcium fluorite (in which case the presence of two-level systems has been established experimentally) and alumomagnesium spinel, there is a deviation of the composition from stoichiometry because of the presence of a certain number of oxygen vacancies. In the $Y_{3-x}R_xAl_5O_{12}$ crystals, for example, the number of oxygen vacancies is estimated[10] to be 10^{20} cm^{-3}. Some of these vacancies are also associated with the incorporation of several ions in interstitial positions. These vacancies are eliminated during an annealing, as the interstitials and vacancies are annihilated. Annealing $Y_{3-x}Er_xAl_5O_{12}$ crystals for 10 h at 1200 °C leads to a significant shift of the second maximum of the signal toward a shorter arrival time, while the basic features characteristic of the slow transport of slightly nonequilibrium phonons are retained. It can thus be suggested that the formation of two-level systems is associated with the presence of vacancies on oxygen polyhedra which coordinate the a, c, and d sites in the garnet lattice. It is natural to assume that these vacancies are distributed among the dodecahedra which coordinate the sites of the yttrium Y and R atoms in proportion to the composition. In other words, the vacancy concentration near R ions would be $(x/3)N_{vac}$. For the mixed crystal $Y_{2.8}Er_{0.2}Al_5O_{12}$, the value $N_{vac} = 10^{20}$ leads us to $6 \cdot 10^{18}$ cm^{-3}, which is fairly close to the value used in the numerical estimate. With increasing x, the number of R centers which contain oxygen vacancies in their nearest neighborhood in-

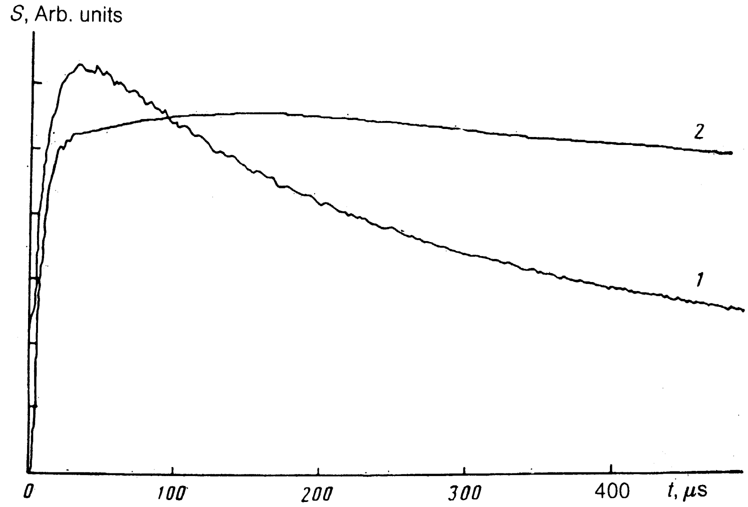

FIG. 9. Signals representing the deviation from a phonon equilibrium in certain samples. 1—CNGG; 2—(10% Er):CNGG. $L_{1,2} = 0.5$ cm, $T = 3.4$ K, $P_H <$ W/mm^2.

creases linearly. The appearance of two-level centers can be attributed to an elastic relaxation in the structure distorted by the presence of the vacancy. The different nature of the propagation of the slightly nonequilibrium phonons in $Y_{3-x}R_xAl_5O_{12}$ may stem from differences in the barrier height and in the size of the energy gap Δ of the two-level centers which arise. Slow transport processes are manifested in crystals containing Er and Ho. Interestingly, among the rare earths the erbium and homium ions have the ionic radii closest to that of the yttrium ion (the ionic radius of $Y^{3+} = 1.01$, that of $Er^{3+} = 1.0$, and that of $Ho^{3+} = 1.02$; for all other R^{3+} ions, the difference between the ionic radii of R^{3+} and Y^{3+} is larger). The reason why there are no slow transport processes of slightly nonequilibrium phonons in other mixed RE:YAG crystals may be a larger value of Δ due to a greater deformation of the structure. In a nonstoichiometric crystal matrix, there is the further possibility that Raman-pumping effects are not manifested because of the absence of a strong elastic scattering (because of the condition $l_R \gg L$).

Let us summarize the results of this study. Our study of the propagation of slightly nonequilibrium phonons in mixed crystals has made it possible to distinguish and study processes of a new type, which are responsible for a transport of excitations: "slow" energy-transport processes. The features observed in the signal propagation for various mixed crystals ($MgAlO_4$:Mn, $Y_3Al_5O_{12}$:Ho, $Gd_3Ga_5O_{12}$:Er, $Y_3Al_5O_{12}$:Er, and $Ca_3Nb_{1.69}Ga_{3.20}\Box_{0.11}O_{12}$:Er) are evidence that slow transport processes play an important role. All the basic features of the propagation of slightly nonequilibrium phonons in these crystals can be explained satisfactorily by a model which assumes the existence of a small number of two-level centers, with a concentration $N_{2LS} \simeq 10^{18}$–10^{20} cm^{-3}, with an energy gap of several kelvins, in these crystals. According to this model, the reason why energy transport is slowed down in these crystals is a redistribution of energy between the heat pulse and the system of two-level centers, as a result of a Raman pumping of centers by phonons. A study of the propagation of slightly nonequilibrium phonons in mixed crystals may thus prove to be a useful method for describing the transition from the crystalline state to the disordered state.

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