Investigation of solutions of yttrium-erbium aluminum garnets by the method of propagation of nonequilibrium phonons and spin relaxation

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An investigation was made of the propagation of nonequilibrium phonons in solid solutions of yttrium-erbium aluminum garnets. Certain features of the propagation of nonequilibrium phonons were attributed tentatively to the paramagnetic nature of the Er^{3+} ions. Experiments on spin-lattice relaxation revealed a new level of Er^{3+} in the garnet lattice and yielded the energy position of this level (≈ 4.5 K).

Propagation of nonequilibrium phonons in insulating crystals with impurities, including substitutional solid solutions, is now better understood.[1] It has been shown[2] that in solid solutions of yttrium-rare-earth aluminum garnets $Y_{3-x}R_xAl_5O_{12}$, where R = Lu, Dy, Yb, Tb, ... (YAG:R) the nature of nonequilibrium phonons in crystals with substitutional impurity concentrations $x \ll 3$ or $3 - x \ll 3$ is practically independent of the nature of the impurity and is governed by the Rayleigh mechanism of the scattering by defects associated with the difference between the masses of yttrium and of the rare-earth metal ion. Substitutional ions have included nonparamagnetic Lu^{3+} and paramagnetic Dy^{3+}, Tb^{3+}, and Tm^{3+} ions, for which the system of low-lying Stark levels can generally be excited by injection of nonequilibrium phonons.

Under our experimental conditions we found no singularity ties associated with the paramagnetic nature of the substitutional impurity, until Er was used as this impurity. The characteristic features of the propagation of nonequilibrium phonons in $Y_{3-x}Er_xAl_5O_{12}$ samples were the subject of the present study.

We used the experimental method described in detail in Refs. 2 and 3. Nonequilibrium phonons were excited by heating (with a current pulse of 70-ns duration) a film of gold deposited by thermal evaporation on the end face of a sample. An In or Sn bolometer was used to record the signal on the opposite face of a sample at the superconducting transition temperature of the gold film. When the change in the temperature of the thermostat was altered, the superconducting transition region was shifted by the application of a weak magnetic field of ~ 100–300 Oe intensity.

We determined the time of arrival of a maximum and the profile of the phonon nonequilibrium signal in YAG:Er samples. Samples of YAG:Er were prepared by horizontal directional crystallization and were taken from two independent sources. The results for the two batches of samples were identical. If necessary, parallel measurements were made on YAG:Lu samples, because a comparison with these made it possible to identify readily the characteristics of propagation of nonequilibrium phonons in YAG:Er. The Er concentration was within the range $0.1 \leqslant x \leqslant 3$ and the thermostat temperature T_0 was 2–3.8 K.

Propagation of nonequilibrium phonons in samples of YAG:R solid solutions had been investigated earlier,[3] where the power density released in a heater and needed to realize a particular regime of propagation of nonequilibrium phonons was determined as a function of the sample dimensions, impurity concentration, thermostat temperature, and heat removal conditions. In most of our experiments the power density released in the gold film of the heater did not exceed 0.1 W/mm^2. Under these conditions we expected the diffusion regime involving elastic scattering of nonequilibrium phonons by the difference between the masses of the host and substituted ions. In the case of the samples which were in contact with liquid helium we observed the nonequilibrium phonon diffusion regime right up to power densities 0.2–0.3 W/mm^2.

When the power density released in the heater in contact with liquid helium was limited to a few hundredths of a watt per square millimeter, the rise in the temperature of the heater relative to the thermostat temperature should not exceed a few tenths of 1 K (Ref. 4). When the arrival time of the phonon nonequilibrium maximum t_M was determined under these conditions for samples kept at different thermostat temperatures, we obtained the $t_M(T)$ dependence on the assumption that nonequilibrium phonons were propagated and that these phonons had the Planck distribution with a temperature $T_h \approx T_0$ in the heater film.

Figure 1 shows on the same time scale the signals obtained from a bolometer in the case of propagation of nonequilibrium phonons in samples of $Y_{2.8}Lu_{0.2}Al_5O_{12}$ (1) and $Y_{2.8}Er_{0.2}Al_5O_{12}$ (2) of identical length when the power density released in the heater was the same, $P_h = 0.02$ W/mm^2. The main difference between curves 1 and 2 in Fig. 1 is the appearance of a wide second maximum in the case of YAG:Er; the arrival time of the second maximum at $T = 3.8$ K was $t_{M2} \geqslant t_{M1}$; $t_{M2} \geqslant 10^{-4}$ s. A comparison of curves 1 and 2 indicates that nonequilibrium phonons forming the maximum of a signal in YAG:Lu made the dominant contribution to the second maximum in YAG:Er. Similar measurements were carried out on a garnet sample with the composition $Gd_{2.85}Er_{0.15}Ga_5O_{12}$, where again a second diffusion maximum with $t_{M2} \geqslant 10^4$ s was readily observed and this provided convincing evidence that the effects observed were associated with the presence of Er in the garnet lattice.

We investigated the "diffuseness" of the motion of phonons forming both nonequilibrium maxima. The arrival time of the maximum of nonequilibriun phonons traveling in a sample under diffusion conditions was $t_M \propto L^2/D$, where D is the diffusion coefficient for phonons of frequency ω_0 forming the maximum of the recorded signal. In the analysis of the experimental results the dependence $t_M \propto L^2$ was regarded as the main criterion of the diffusion of nonequilibrium phonons. In the case of YAG:Lu and YAG:Er samples it

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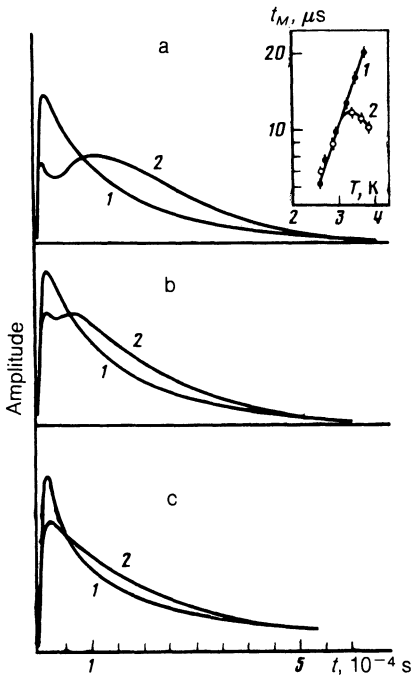

FIG. 1. Time dependences of the signals recorded with a bolometer when nonequilibrium phonons propagated in samples of length $L = 0.68$ cm: 1) $Y_{2.8}Lu_{0.2}Al_5O_{12}$; 2) $Y_{2.8}Er_{0.2}Al_5O_{12}$. Thermostat temperature: a) $T = 3.8$ K; b) 3.12 K; c) 2.51 K. Heater power density $P_h = 0.02$ W/mm^2. The inset shows the dependence of the arrival times of the maxima of the signal on the temperature of the heater $T_h \approx T_0$ for the same two samples: 1) $Y_{2.8}Lu_{0.2}Al_5O_{12}$; 2) first maximum for $Y_{2.8}Er_{0.2}Al_5O_{12}$.

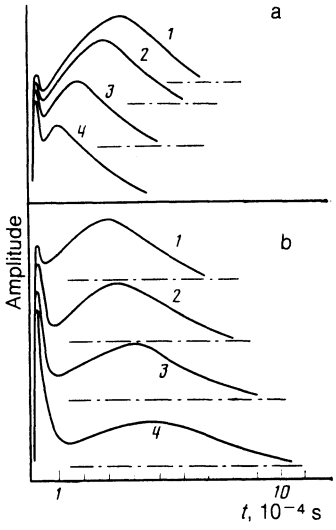

FIG. 2. Time dependences of the signal recorded by a bolometer and due to propagation of nonequilibrium phonons at various temperatures: a) $Y_{2.4}Er_{0.6}Al_5O_{12}$ $L = 0.87$ cm, $P_h = 0.06$ W/mm^2, $T = 3.82$ K (1), 3.66 K (2), 3.44 K (3), and 3.25 K (4); b) $Er_3Al_5O_{12}$, $L = 0.4$ cm, $P_h = 0.1$ W/mm^2, $T_0 = 3.8$ K (1), 3.37 K (2), 3.07 K (3), and 2.67 K (4). The dash-dot lines represent the zero reading of the bolometer.

was also found that the first maximum obeyed $t_{M1} \propto L^2$ (see also Ref. 3). The second maximum in the case of YAG:Er obeyed $t_{M2} \propto L^{1.8-2}$ at the limits of the investigated range of impurity concentrations $x \leqslant 0.3$ and $x \geqslant 2.7$; in the range $0.3 < x < 2.7$ we found that $t_{M2} \propto L^{1.6-1.8}$. These results indicate that in the case of the second maximum exhibited by YAG:Er samples there was some (although not very great) deviation of the motion of nonequilibrium phonons from the diffusion laws describing the motion of noninteracting particles scattered elastically by defects. Clearly, there was some contribution of inelasticity which might be due to the interaction with two-level systems.

Assuming that the deviation from the diffusion-type motion was small, we tried to obtain quantitative characteristics of the scattering of nonequilibrium phonons because in the diffusion case we should have $t_M \propto D^{-1} \propto \tau_0^{-1}$, where τ_0 is the elastic scattering time of nonequilibrium phonons. We plotted in Fig. 1 (see the inset) the temperature dependences of the arrival of the maxima of the signal in samples of YAG:Er and YAG:Lu. In the case of YAG:Lu we found a dependence $t_M \propto T^4$, which was attributed in Ref. 4 to the Rayleigh scattering of nonequilibrium phonons by the difference between the masses of the host and substituted atoms. In the case of YAG:Er this dependence was not obeyed by the first maximum, particularly at "high" temperatures of 3–3.8 K. These results (together with the data of Fig. 1) demonstrated, in our opinion, that phonons with typical energies ω_0, responsible for the maximum of the recorded signal t_{M1} in the case of YAG:Lu and for the first maximum in the case of YAG:Er, were transferred to the region of the second maximum characterized by the arrival time t_{M2}. The transfer of phonons was more effective at higher temperatures T_0. A more detailed comparison of the maxima in the case of YAG:Lu and of the first maximum in the case of YAG:Er indicated that in the latter case it was shifted to the left along the time axis, i.e., it was due to phonons characterized by a lower frequency (lower temperature).

The "enrichment" of the first diffusion maximum with low-frequency phonons increased on increase in the Er concentration. In the range $x \gtrsim 0.6$ we observed a tendency (Fig. 2) for the conversion of the first diffusion maximum into a ballistic signal; only the second maximum with the longer delay time $t_{M2} > 10^{-4}$ s is due to diffusion.

The results plotted in Figs. 2a and 2b made it possible to follow the temperature dependence of the arrival time of the second maximum in the case of YAG:Er. It depended on the erbium concentration. For samples with $x < 0.6$–0.75 (Figs. 1a and 2a) the arrival time t_{M2} increased with temperature. This dependence could be represented in the form $t_{M2} \propto T_0^7$ or $t_{M2} \propto \exp(-\Delta/T)$, where $\Delta = 28$–30 K. (In our experiments we used a temperature interval which was far too narrow to decide reliably between one of these temperature dependences.) A further increase in the impurity concentration to $x \gtrsim 1$ changed drastically the temperature dependence of t_{M2} (Fig. 2b): the value of t_{M2} began to decrease on increase in temperature: $t_{M2} \propto T^{-n}$ ($n = 1$–1.5).

We investigated the behavior of the signals for YAG:Er samples with different concentrations at $T = \text{const}$; the lengths of the samples and the values of l_h/L, where l_h is the linear size of the heater, were selected to be the same. As the Er^{3+} concentration was increased, the relative weight and the arrival time of the second maximum increased. In the range $x \geqslant 0.6$ the response curve of the bolometer consisted practically only of the second maximum, whereas the first maximum was converted into a narrow ballistic peak, as mentioned above (see also Figs. 2a and 2b). Figure 3 shows the dependence of t_{M2} on the Er concentration in the garnet

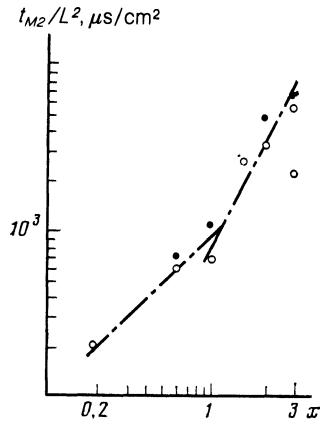

FIG 3. Dependence of t_{M2} on the composition of $(Y-Er)_3Al_5O_{12}$ solid solutions, $P_h = 0.1$ W/mm², $T_0 = 3.8$ K: ○) $Y_{3-x}Er_{3-x}Al_5O_{12}$; ●) $Y_{3-x}Er_xAl_{1.95}Sc_{0.05}(AlO_4)_3$.

lattice. For $x \leqslant 1$ the dependence was linear, whereas for $x > 1$ it was proportional to x^2.

These experimental results suggested that the appearance of the second diffusion peak in the signal obtained for YAG:Er samples was due to the paramagnetic nature of the Er^{3+} ions and the associated appearance of an allowed level (or a system of levels) in the spectrum of electronic states: the energies of the new levels were typical of phonons which would form a diffusion maximum under the Rayleigh scattering conditions in, for example, YAG:Lu. The existence of a system of low-energy levels, which could be called a miniband and which could be perturbed by the participation of a large number of phonons injected from the heater (Figs. 1 and 2), was in the final analysis responsible for the second maximum in the bolometer response.

This hypothesis was checked in a study of the coupling between the system of the Er^{3+} ions and the phonons. The Er^{3+} ions in YAG were characterized by an effective spin $S' = 1/2$ and the principal values of the g tensor were $g_x = 3.71$, $g_y = 7.75$, and $g_z = 7.35$ (Ref. 5). The rms value of the local field ω_L, due to the magnetic dipole interactions between the Er^{3+} ions, reached $\sim 10^{11}$ s^{-1} at the impurity concentrations used in our study. This made it possible to observe paramagnetic absorption of centimeter electromagnetic waves, corresponding to spin transitions in local fields in the absence of an external static magnetic field. The microwave field energy which was then absorbed reached a quasiequilibrium dipole-dipole reservoir (DDR) of the Er^{3+} ions.[6]

The coupling between the DDR and phonons could be direct, at frequencies of the order of ω_L, but it would involve a higher energy level separated by the Stark splitting Δ from the ground state. In the latter case a theoretical expression for τ_{dl} of the spin-lattice relaxation time of the DDR, obtained from the results of Ref. 7, was described by

$$\tau_{dl}^{-1} = \frac{3A\Delta^3}{2\pi\bar{v}^3}\frac{M_2}{\omega_L^2}\frac{1}{\mathrm{sh}(\Delta/T)}, \qquad (1)$$

where $\bar{v}$ is the average velocity of sound, A is the spin-phonon coupling constant, and M_2 is the second moment of the spin-phonon interaction line at the frequency Δ. (Such a dependence had been observed earlier[8] for $Al_2O_3:Cr^{3+}$ crystals.) Clearly, if $\Delta > T$, Eq. (1) gives rise to an exponential dependence with an argument $(-\Delta/T)$. It should be stressed that in the presence of several types of paramagnetic centers in a sample all of them contributed to relaxation of the overall dipole reservoir.

We investigated spin-lattice relaxation of the DDR and observed the process of recovery of equilibrium absorption after its saturation with a high-power microwave pulse. These experiments were carried out at a frequency 9.4 GHz at temperatures 1.5–4.2 K in the absence of an external magnetic field. The possible role of the "phonon bottleneck," i.e., of the accumulation of nonequilibrium phonons in the course of relaxation,[5] was determined by investigating samples of two types: $0.5 \times 1 \times 1$ mm crystals and a powder prepared from them (the use of a powder was possible because of the absence of the anisotropy effects in zero magnetic field).

In both cases the process of relaxation could be represented by a simple exponential function with a characteristic time τ_{dl}. The temperature dependences of τ_{dl} obtained for different Er^{3+} concentrations are plotted in Fig. 4. They were described well by the formula

$$\tau_{dl}^{-1} = B\exp(-\Delta_1/T) + C\exp(-\Delta_2/T), \qquad (2)$$

and we found that for all the samples we had $\Delta_1 = 28.8$ K. On the other hand, the value of Δ_2 differed for powders and crystals; in the former case it was 4.5 K for all impurity concentrations, whereas in the case of crystals it varied from 4.5 K for $x = 0.2$ to 7–10 K for $x \geqslant 0.6$.

The agreement between Δ_1 and the known energy of an excited level $^4I_{15/2}$ of the Er^{3+} ions in YAG confirmed convincingly our theory. The presence of the second exponential function in Eq. (2) indicated an additional new level with an energy 4.5 K which was clearly responsible for the second maximum in Fig. 1.

The dependence of τ_{dl} on the dimensions of a sample

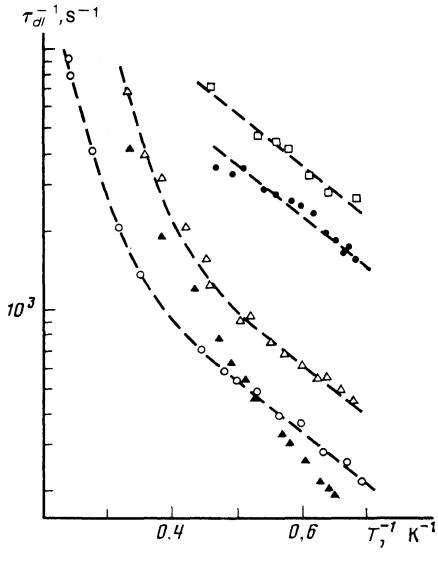

FIG. 4. Dependences of the rate of relaxation of the dipole-dipole reservoir on the reciprocal of temperature obtained for powders of $Y_{3-x}Er_xAl_5O_{12}$ ($x = 0.2$, 0.6, 1, and 3, represented by ○, △, □, and ●) and in a crystal ($x = 0.6$, denoted by ▲). The dashed curves are the dependences described by Eq. (2) with suitably selected parameters B and C.

(with different results for powders and crystals) observed in the range $x \geqslant 0.6$ indicated that a phonon bottleneck appeared in the temperature range where the DDR relaxation was governed by the participation of phonons with energies ≈ 4.5 K. The apparent increase in Δ_2 by a factor of 1.5–2 was then due to delay of the transfer of excitation from phonons to the helium bath because of the repeated capture ("trapping") of phonons and their reemission at paramagnetic centers.[9] Since the dimensions of the samples in the experiments on the propagation of nonequilibrium phonons were $1 \times 1 \times 1$ cm, the trapping of phonons by the level with the energy 4.5 K could in this case be even more effective.

It should also be mentioned that the proximity of the values of Δ in the temperature dependence of t_{M2} (Figs. 1a and 2a) to Δ_1 [see Eq. (2)] might not be accidental and could be associated with the mechanism of relaxation of a miniband excited by phonons.

The spin relaxation method made it possible to identify a new level of Er^{3+} with the energy $\Delta_2 = 4.5$ K in the garnet lattice, so that the motion of nonequilibrium phonons could now be described qualitatively as follows: phonons injected into a sample of YAG:Er excited the spin subsystem of Er^{3+} ions characterized by $\Delta_2 = 4.5$ K. The minimum widths of the ground and excited levels (minibands) were governed by the magnetic dipole-dipole interaction and amounted to $\hbar\omega \approx kT \approx 1$ K. Therefore, the excitation occurred at phonon frequencies $\omega \sim \omega_L \approx 1$ K and $\omega \approx \Delta_2 \pm \omega_L = 3.5$–$5.5$ K.

This excitation could be regarded as the interaction of nonequilibriun phonons with a set of two-level electron systems of paramagnetic nature. The bulk of the phonons was in fact "trapped" within a miniband in the region of $\Delta_2 = 4.5$ K and the relaxation of these two-level systems was recorded by a bolometer after a long delay relative to the usual Rayleigh scattering time (trapping effect). Cooling shifted the maximum of the distribution of the injected nonequilibrium phonons outside the range of the effective (resonance) interaction with this miniband and the proportion of the phonons responsible for the second maximum decreased (Figs. 1a, 1b, 2a, and 2b).

If the proposed qualitative description is correct, the following conclusion important for the kinetics of phonons in crystals with a large number of scattering centers can be deduced: the arrival time of the phonon nonequilibrium maximum in the case of diffusive motion is determined by phonons of frequencies (temperatures) close to the temperature of the thermostat and not at $T = 2.8T_0$, as assumed within the limits of very weak scattering in samples characterized by $x \ll 1$.

The physical reasons for the appearance of an additional level with $\Delta_2 = 4.5$ K are not yet clear. In all probability it is not associated with the energy of the Stark level of an Er^{3+} ion occupying an Al site in the octahedral coordination (due to excess of erbium amounting to 1–2% instead of Al). Measurements on YAG:Er:Sc samples (when Sc displaced effectively Er from the Al positions) failed to reveal significant changes in the characteristics of propagation of nonequilibrium phonons (see, for example, Fig. 3) or in the spin-phonon relaxation time. A recent investigation[10] revealed new paramagnetic erbium centers in YAG and these had very different parameters from the known Er^{3+} centers; the relative concentration of the new centers was not very high, but it increased on increase in the total concentration of Er. It was concluded in Ref. 10 that the Er_{II}^{3+} centers observed by them occupied the usual yttrium sites of the defect in the immediate environment. The additional level found by us could also be associated with centers of this type. In particular, after prolonged (~ 10 h) annealing of YAG:Er samples in air at 1200 K, which should "heal" the structure defects, we found that the arrival time of the second maximum t_{M2} decreased for some of the crystals, i.e., the new states of Er assumed a lesser role in the propagation of nonequilibrium phonons.

However, irrespective of the nature of the new level, its existence was of fundamental importance, because it allowed us to propose (as was done above) a working model for propagation of nonequilibrium phonons in YAG:Er when, in addition to the elastic scattering process, these phonons interacted also with two-level systems of paramagnetic origin. We would regard the proposed model as the starting point for further investigations which would require additional experiments and a careful theoretical analysis.

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