A narrow phonon neck in the luminescence of CaF_2-Eu^{2+} crystals and the anharmonic lifetime of terahertz acoustic phonons

A. V. Akimov, A. A. Kaplyanskiĭ, and A. L. Syrkin
A. F. Ioffe Physicotechnical Institute, USSR Academy of Sciences

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A narrow phonon neck has been detected in the $d \rightarrow f$ fluorescence of CaF_2-Eu^{2+} crystals from the $\Gamma_8^+(4f^6 5d)$ state split by deformation. The mode-averaged anharmonic lifetime of the 2-THz acoustic phonons in fluorite was determined from the fluorescence kinetics $\tau_p \approx 2 \times 10^{-7}$ sec.

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The anharmonic lifetime of terahertz-range (10^{12} Hz) acoustic phonons is very difficult to determine experimentally, which accounts for the paucity of existing experimental estimates.[1] In this study we have determined the lifetime of terahertz acoustic phonons from the fluorescence kinetics of activated crystals with a "narrow phonon neck." We have selected uniaxially strained CaF_2 - Eu^{2+} crystals, which have been widely used in studying high-frequency acoustic phonons in crystals.[2–5]

The $6 \times 1.5 \times 1.5$-mm, parallelepiped CaF_2 - 0.01% Eu^{2+} single crystals were subjected to a uniaxial, elastic compression along the [001] axis at $T = 1.5$ K. The strain causes a doublet splitting of the lower Γ_8^+ level of the excited $4f^6$ $5d$ configuration of Eu^{2+} (Fig. 1).[6] The maximum splitting $\Delta = W_2 - W_1$ may reach 70 cm^{-1}. The sample was excited through the side face by an N_2 pulsed laser beam ($\lambda = 3370$ Å, pulse duration ≈ 10 nsec, repetition frequency 100 Hz, pulse power $P = 1$ kW, diameter of focused beam $L = 0.3$–0.6 mm). The excited volume was projected by means of a light pipe on the slit of the DFS-24 spectrometer, which separated the spectral $d \rightarrow f$ luminescence lines of Eu^{2+} from both W_1 and W_2 sublevels. The time dependence of the fluorescence pulses $I_1(t)$ and $I_2(t)$ was measured by using the photon-counting method and storage of signals.

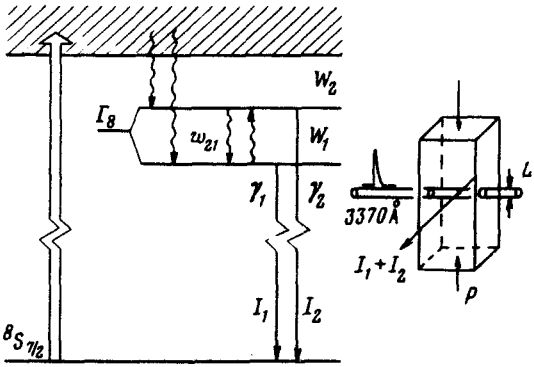

FIG. 1. Schematic of the experiment.

The experiments were based on the following concept. Both of the deformation levels W_1 and W_2 are populated in the process of nonradiative relaxation from the upper states (Fig. 1). The probability of the $W_2 \to W_1$ transition with the emission of a resonance phonon $\hbar\omega = \Delta$, which is $w_{21} = 10^{11}$ sec^{-1} [for $\omega = 10$-30 cm^{-1} (Ref. 5)], greatly exceeds the probability of γ_2 radiative $d \to f$ transition with W_2 [$\gamma_2^{-1} \approx \gamma_1^{-1} = 0.6$ μsec (Ref. 7)]. Therefore, the Eu^{2+} ions will go from W_2 to W_1 in a time $\ll 1$ nsec, with the emission of acoustic phonons $\hbar\omega = \Delta$ into the lattice.[2,4] The optical excitation of Eu^{2+} to the Γ_8^+ ($4f^6\ 5d$) state is therefore accompanied by an injection of phonons into the excited volume, which interact resonantly with the W_1 and W_2 two-level system. The density of these nonequilibrium phonons can be high, since their yield from the excited volume is complicated by nonresonance (Rayleigh) scattering by the impurity centers and defects.[8] Under these conditions the multiple absorption-emission ($W_1 \rightleftarrows W_2$) of nonequilibrium phonons $\hbar\omega = \Delta$ determines the population N_2 of the W_2 level ("narrow phonon neck"). It follows from the balance equations that if the occupation numbers of the nonequilibrium phonons are small ($\bar{n}_\omega \ll 1$),

$$\frac{I_2(t)}{I_1(t)} = \frac{\gamma_2 N_2(t)}{\gamma_1 N_1(t)} \approx \bar{n}_\omega(t). \tag{1}$$

The kinetics of the departure of phonons from the active volume, in particular, the role of the finite lifetime of phonons can be investigated by measuring the time dependence of the ratio I_2/I_1.

The measurements showed that a narrow phonon neck can indeed be observed in the experiments. The ratio of the fluorescence pulse amplitudes (I_2^0/I_1^0) increases with the power P of the exciting light, where $I_1^0 \sim P$. This is consistent with (1) ($\bar{n}_\omega$ increases with P) and clearly indicates that superabsorption of relaxation phonons $\hbar\omega = \Delta$ plays an important role in the population of the W_2 level. Insufficient stability of the nitrogen layer made it impossible to measure the dependence of I_2^0/I_1^0 on P. The absolute value of I_2^0/I_1^0 reaches 0.01-0.1 at $P_{max} \approx 1$ kW; the initial occupation numbers of the injected phonons under these conditions were $\bar{n}_\omega^0 = 10^{-2}$-$10^{-1}$.

Figure 2 shows the typical pulses $I_1(t)$ and $I_2(t)$ for two splitting values Δ. We can see that the damping time τ_2 of $I_2(t)$ depends strongly on Δ. The observed

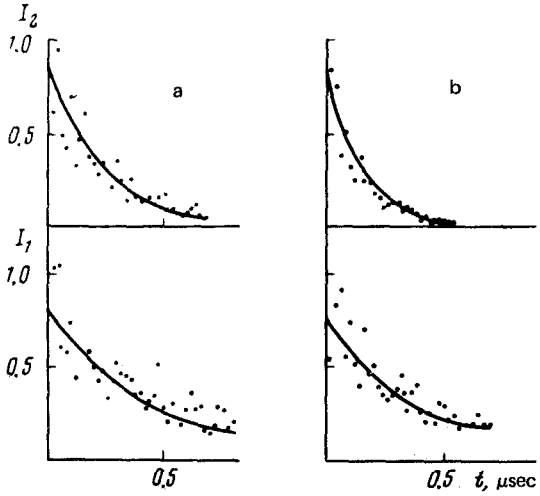

FIG. 2. Luminescence pulses of the upper (I_2) and lower (I_1) Γ_8^+ sublevels. (a) $\Delta = 14$ cm^{-1}, (b) $\Delta = 60$ cm^{-1}.

damping times $\tau_2 \approx 0.1$-0.25 μsec greatly exceed the lifetime of the W_2 level relative to the single-phonon decay $W_2 \to W_1$ ($\omega_{21}^{-1} \approx 10^{-11}$ sec). This again indicates the role the relaxation phonons play in the population of W_2. The time τ_2 also depends (at $\Delta \approx 20$-50 cm^{-1}) on the size of the excited volume (the diameter L of the laser beam). It is important to emphasize that τ_2 is independent of pumping P.

The damping time τ_1 of I_1 (t), which varies as a function of Δ and of L in the range 0.32-0.5 μsec, is noticeably larger than τ_2. The value of τ_1 is close to the known[7] radiation lifetime γ^{-1} of the Γ_8^+ level, which, in principle, determines the damping of the W_1 level. The observed τ_1 value can be influenced by the reabsorption of the optical radiation in the line,[7] which is probably responsible for the dependence of τ_1 on L and partly on Δ (through the nonuniform broadening of the spectral line $W_1 \to {}^8S_{7/2}$ due to deformation, which influences the reabsorption). The other possible reason for the dependence of τ_1 on Δ is the decrease of the probability of γ_1 due to deformation mixing of the W_1 state with the "optically inactive" Eu^{2+} state which is located ~ 15 cm^{-1} above the Γ_8^+ state.[6]

Thus a study of the relative intensity (I_2^0/I_1^0) and the kinetics of fluorescence shows that the population of W_2 is determined by the relaxation phonons $\hbar\omega = \Delta$ that are injected into the excited volume. The time dependence of the occupation numbers $\bar{n}_\omega$ of phonons in the excited volume was calculated from the I_1 (t) and I_2 (t) dependences according to (1), and the appropriate damping time τ of phonons in the volume was determined. Figure 3 is a plot of τ as a function of Δ for two sizes of the volume. The phonon yield $\hbar\omega$ from the volume occurs through spatial diffusion (with the time τ_d) and through anharmonic decay (time τ_{decay}), so that $\tau^{-1} = \tau_d^{-1} + \tau^{-1}$. The dependence of τ on the volume's size (Fig. 3), observed at $\Delta = 20$-50 cm^{-1}, shows that the spatial diffusion of phonons from the volume is considerable in this frequency range. The fact that τ is independent of the pump power P (i.e., of

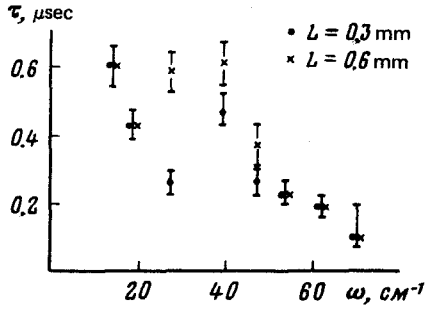

FIG. 3. Decay time of phonons in an excited volume, plotted as a function of frequency.

the number of excited Eu^{2+} ions) shows that this diffusion is not associated with the resonance scattering of phonons by the Eu^{2+} ions excited to the Γ_8^+ state, but is rather attributed to nonresonance Rayleigh scattering by impurities and defects of the CaF_2 lattice.[1)] In the last case $\tau_d \sim \omega^4$; the time τ_d can be greater than τ_{decay} when ω is large, and then τ is determined by the lifetime of phonons τ_{decay}. This can account for the independence of τ of L at frequencies $\omega > 50$ cm^{-1} (Fig. 3); the corresponding experimental time $\tau \approx 2 \times 10^{-7}$ sec for phonons $\omega = 2$ THz is the anharmonic lifetime τ_{decay} averaged over the phonon modes.

According to existing ideas,[1] the phonon decay proceeds primarily via the short-lived LA phonons, whereas the TA phonons are relatively stable. In this case $\tau_p^{-1} = \tau_L^{-1}/1 + (v_L/v_t)^3$, where τ_L is the decay time of LA phonons and the denominator takes into account the different density of states of LA and TA phonons (v_L and v_t are the corresponding velocities of sound). $\tau_L \approx 1/8\ \tau_{decay} \approx 2.5 \times 10^{-8}$ sec for CaF_2. This value is 6 to 7 fold higher than the theoretical estimate of the lifetime of the 2-THz LA phonons relative to the $L \to L + T$ decay.[2)]

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[1)]This is the main difference between it and the "resonance" capture of 29-cm^{-1} phonons in $Al_2O_3Cr^{3+}$.[9,10]

[2)]The calculations were performed by V. D. Polikarpov.

1. W. E. Bron, Phys. Rev. **B21**, 2627 (1980).
2. W. Eisfeld and K. F. Renk, Appl. Phys. Lett. **34**, 481 (1979).
3. A. P. Abramov, I. N. Abramova, I. Ya. Gerlovin, and I. K. Razumova, Fiz. Tverd. Tela **22**, 946 (1980) [Sov. Phys. Solid State **22**, 556 (1980)].
4. A. V. Akimov, A. A. Kaplyanskiĭ, and A. L. Syrkin, Pis'ma Zh. Eksp. Teor. Fiz. **32**, 136 (1980) [JETP Lett. **32**, 124 (1980)].
5. A. V. Akimov and A. A. Kaplyanskiĭ, Zh. Eksp. Teor. Fiz. **80**, 767 (1981).
6. A. A. Kaplyanskiĭ and A. K. Przhevuskiĭ, Optika i spektroskopiya **19**, 597 (1965).
7. P. Kisliuk, H. H. Tippins, and C. A. Moore, Phys. Rev. **171**, 336 (1968).
8. W. E. Bron and W. Grill, Phys. Rev. **B16**, 5303,5315 (1977).
9. K. F. Renk and L. Deisenhofer, Phys. Rev. Lett. **26**, 764 (1971).
10. A. A. Kaplyanskiĭ, S. A. Basoon, and V. L. Shektman, in "Light Scattering in Solids," ed. J. L. Birman, H. Z. Cummins, and K. K. Rebane, N.Y., 1979, p. 95.

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