Observation of resonant relaxation of acoustic phonons by vibronic anti-Stokes luminescence in doped crystals

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We report experiments on the direct observation of nonequilibrium acoustic phonons generated in the nonradiative relaxation of electronic excitation of the impurity ions in the doubly activated crystals CaF_2–Eu^{2+}, Sm^{2+}. Resonant phonons at ~1 THz given off in transitions between the electronic levels of the Eu^{2+} ion are detected by the vibronic luminescence of the Sm^{2+} ion.

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Recent papers[1,2] have indicated the possibility of using the acoustic vibronic luminescence of activated crystals [SrF_2–Eu^{2+} (Ref. 1), CaF_2–Sm^{2+} (Ref. 2)] for recording the spectrum of nonequilibrium acoustic phonons in the terahertz range [a vibronic phonon spectrometer (VPS)]. In this letter we report the first use of a VPS for a detection of the nonequilibrium acoustic phonons arising in a crystal during nonradiative relaxation of optically excited impurity ions.[3] We used CaF_2 crystals with two activators (Eu^{2+} and Sm^{2+}) and detected the resonant phonons given off in transitions between the electronic levels of Eu^{2+} by means of the anti-Stokes vibronic luminescence of the Sm^{2+} ions.

Oriented single-crystal samples[1)] of CaF_2–Eu^{2+}, Sm^{2+} with dimensions of $5\times1\times1$ mm were placed in liquid helium ($T=2$ K) and subjected to a uniaxial compression along the [001] axis. The Eu^{2+} ions (ground state $4f$, $^8S_{7/2}$) were excited continuously to the higher states of the mixed configuration $4f^65d$ by illumination of the sample with the 365 nm line of mercury (DRSh-250 tube with FS-7 filter). The lowest electronic level of the excited $4f^65d$ configuration (24206 cm^{-1}) is split by the deformation into a doublet W_2, W_1 with a width $\Delta = W_2 - W_1$ which can vary depending on the size of the compression **p** (see Fig. 1).[4] The nonradiative relaxation of an excitation at Γ_8 (W_2, W_1) in a relaxation channel including the single-phonon transitions $W_2 \to W_1$ should involve the efficient emission of resonant phonons of frequency $h\omega = \Delta$ into the lattice.[5]

For detecting the excess concentration of these relaxational phonons, we used the $d \to f$ luminescence of the Sm^{2+} ions at the electronic transition $\Gamma_1^-(4f^55d$, 14373 $cm^{-1}) \to \Gamma_4^+(4f^6, {}^7F_1$, 263 $cm^{-1})$. This transition contributes a phononless line at 7085Å (at $\mathbf{p} = 0$) to the spectrum at $T = 2$ K, as well as an intense vibronic wing of this line in the Stokes region.[6,7] The Sm^{2+} luminescence was excited under steady-state conditions by the 4880 and 5145 Å lines of the argon laser (these lines are not absorbed by the Eu^{2+} ions). In accordance with the basic idea of the vibronic phonon spectrometer,[1,2] it was assumed that the relaxation phonons $h\omega = \Delta$ will give selective amplification of the stationary intensity of the vibronic anti-Stokes wing at a frequency sepa-

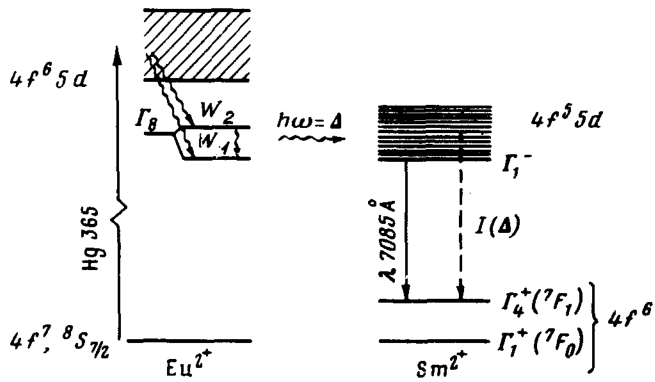

FIG. 1. Schematics of generation and detection of relaxational phonons in the crystal CaF_2–Eu^{2+}, Sm^{2+}.

ration of Δ from the phononless line of Sm^{2+}.

In the experiments, we investigated how additional illumination of the crystal by the 365 nm line of mercury, which leads to excitation of the Eu^{2+} ions, affects the stationary spectrum of anti-Stokes luminescence of Sm^{2+} in the region of the $\Gamma_1^- \to \Gamma_4^+$ line, which is excited by the argon laser. (Illumination by the 365 nm line of mercury also causes additional excitation of the Sm^{2+} ions, but the effect of this process is about an order of magnitude smaller than the excitation of Sm^{2+} by the argon laser lines.) The measurements are difficult because of the weakness of the anti-Stokes vibronic luminescence near the phononless line and the presence of radiation of unknown origin in this region that is not due to the vibronic anti-Stokes transition $\Gamma_1^- \to \Gamma_4^+$ in the Sm^{2+} ions. The spectra were obtained by a photon-counting technique using signal storage.

Figure 2 shows the difference spectra $\Delta I^{as}(\omega)$ of the emission in the anti-Stokes

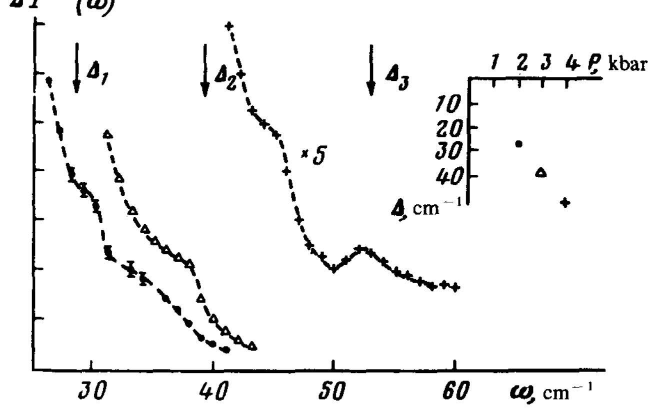

FIG. 2. Anti-Stokes difference spectrum of Sm^{2+} emission for various values of the compressive stress p.

region of the Sm^{2+} phononless line $\Gamma_1^- \to \Gamma_4^+$ for various values of the uniaxial stress. The difference spectrum is $\Delta I^{as}(\omega) = I^{as}(\omega, \mathrm{Hg+Ar}) - I^{as}(\omega, \mathrm{Ar})$, where $I^{as}(\omega, \mathrm{Hg+Ar})$ is the spectrum under simultaneous excitation of the crystal by the 365 nm line of mercury and the argon laser, and $I^{as}(\omega, \mathrm{Ar})$ is the spectrum under excitation of the crystal by the argon laser alone; the frequency ω is measured from the position of the phononless line (which is itself shifted under deformation of the crystal[6]). The right-hand side of Fig. 2 shows the splitting Δ of the Γ_8 level of Eu^{2+} for various values of **p**, as measured according to the position of the long-wavelength component of the split luminescence line $W_1(4f^65d) \to {}^8S_{7/2}(4f^7)$ [see Ref. 4].

It can be seen from Fig. 2 that the difference spectrum $\Delta I^{as}(\omega)$ of the radiation has a distinct maximum, which is shifted to higher frequencies as the compression is increased. The frequency of the maximum coincides with the values of Δ for the doublet splitting of the Γ_8 level of Eu^{2+} at the same values compressive stress (shown by the arrows in Fig. 2). The width of the maximum (2–5 cm^{-1}) agrees with the values of the inhomogeneous broadening of the levels W_2 and W_1 and with the width of the phononless line of Sm^{2+}. It should also be noted that the luminescence spectrum $I^{as}(\omega, \mathrm{Hg})$ in the anti-Stokes region of the phononless line of Sm^{2+} has no features whatsoever at $\omega = \Delta$ under excitation by the 365 nm line of mercury only. Thus, the features of $\Delta I^{as}(\omega)$ are due to the phonons generated by Eu^{2+}.

The intensity of the anti-Stokes vibronic luminescence at frequency ω is[1,2], $I^{as}(\omega) = I^s(\omega)\bar{n}(\omega)$, where $I^s(\omega)$ is the intensity of the Stokes luminescence, and $\bar{n}(\omega)$ is the occupation number for phonons of frequency ω. An estimate by this formula with the measured values of I^{as} and I^s gives $\bar{n} = 10^{-4} - 10^{-5}$ for the occupation numbers of the generated resonant phonons with $\omega = \Delta$. This estimate agrees with the values of $\bar{n}$ obtained independently from the known rate of phonon generation by the Eu^{2+} ions: $\bar{n} = kP\tau\bar{v}^3/12\pi\nu^2 d\nu$, where $P \approx 10^{22}$ $cm^{-3} \cdot sec^{-1}$ is the number of quanta absorbed by the Eu^{2+} ions per unit time per unit volume, $\bar{v} = 3.5 \times 10^5$ cm/sec is the average speed of sound, $\tau \approx 10^{-6}$ sec is the phonon lifetime in the excited volume,[2] $k \approx \frac{1}{2}$ is the quantum yield for the generation of relaxation phonons, and $\nu = 10^{12}$ sec^{-1} and $d\nu = 3 \times 10^{10}$ sec^{-1} are the frequency and width of the generated phonons ($\nu = \omega/2\pi$).

In conclusion, we remark that the combination of different ions in the same volume in doubly activated crystals, with one of the ions generating phonons and the other detecting them, opens up new possibilities for studying the generation and propagation of phonons in the terahertz range in crystals.

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