USE OF PICOSECOND RUBY LASER PULSES IN THE MEASUREMENT OF THE DECAY TIME OF THE LUMINESCENCE BAND OF THE FIRST PHONON REPLICA OF THE A-TYPE EXCITON IN CdS

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The decay time of the luminescence of the first phonon replica of the A exciton in CdS was determined experimentally using a ruby laser operating under longitudinal mode-locking conditions and generating pulses of $\sim 10^{-11}$ sec duration. These pulses were used in the two-photon excitation of the luminescence in CdS and in the determination of the decay time of the first phonon replica band of the A exciton, which was found to be 1.3 nsec.

THE present paper describes an experimental determination of the decay time of a luminescence band in CdS representing the radiative recombination of a free A exciton, which results in the simultaneous emission of a photon and one longitudinal optical phonon. This band is known as the first phonon replica of the A exciton.

The luminescence spectrum of CdS excited by the two-photon mechanism, using a ruby laser radiation at T = 77°K, consists of a green edge luminescence band with its principal peak at $\lambda = 5120$ Å and a blue luminescence band with its center near $\lambda = 4900$ Å.[1] Later investigations[2-4] have established that the blue luminescence band is the first phonon replica band of the free A exciton. It is reported in [2,3] that the stimulated radiation of CdS, excited by the two-photon mechanism at moderately low temperatures, is emitted at the frequency of the first phonon replica of the A exciton. The decay time of the first phonon replica band of the A exciton is estimated to be 10^{-9}–10^{-10} sec.[5] Such very short afterglow times could not have been measured before the advent of lasers emitting pulses of picosecond duration. The availability of picosecond pulses, particularly those generated by ruby lasers working under longitudinal mode-locking conditions,[6,7] has made it possible to demonstrate, using CdS as an example, that these pulses can be used to measure short afterglow times, and thus check experimentally the estimate, given in [5], of the decay time of the luminescence band of the first phonon replica of the A exciton in CdS.

This measurement was made using a ruby picosecond pulse laser[7] as a source of the two-phonon excitation of CdS. The apparatus employed is shown experimentally in Fig. 1. A ruby laser generated a train of picosecond pulses, from which a single pulse was selected by a special shutter.[8] The selected pulse reached a sample of CdS located in a cryostat kept at 77°K. The luminescence of the CdS excited by this ruby laser pulse was directed to an ÉLU-57 photomultiplier, the output signal from which was recorded with one of the beams of a 6LOR-02 fast-response oscillograph. The same oscillograph was used to record simultaneously the exciting radiation pulse, part of which was deflected

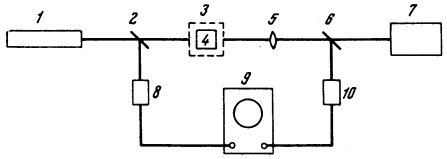

FIG. 1. Schematic representation of the apparatus. 1) Ruby laser generating picosecond pulses; 2), 6) beam splitters; 3) cryostat; 4) CdS sample; 5) lens for imaging the CdS sample on the slit of the ISP-51 spectrograph (7); 8) coaxial photocell; 9) fast-response oscillograph; 10) photomultiplier.

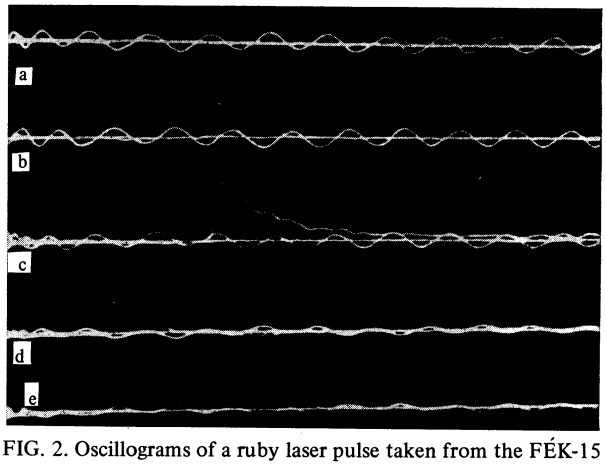

FIG. 2. Oscillograms of a ruby laser pulse taken from the FÉK-15 cell (a) and of pulses excited by ruby radiation: b) blue luminescence of CdS; c) green edge luminescence of CdS. Traces d and e represent a ruby laser pulse taken from the FÉK-15 coaxial photocell (d) and of the same pulse taken from the ÉLU-F7 photomultiplier (e). The period of the sinusoid in all the traces is 10 nsec.

to an FÉK-15 coaxial photocell (Fig. 2a). Some of the CdS luminescence was focused onto the slit of an ISP-51 spectrograph. A suitable interference filter placed in front of the photomultiplier enabled us to select either the green edge luminescence of CdS or the blue band of the first phonon replica of the A exciton.

Since we were interested in the decay time of the first phonon replica band of the A exciton under spontaneous emission conditions, we had to take special

measures to suppress the stimulated emission from the CdS which appeared at $\lambda = 4950$ Å, in spite of the fact that the investigated sample had no specially prepared plane-parallel faces. The suppression was achieved by making all the sides of the CdS sample mat and by reducing the exciting laser radiation with attenuation filters to a value at which laser emission by the CdS sample was no longer observed but at which the sensitivity of the apparatus was still sufficient for quantitative measurements. The absence of laser emission from the CdS was deduced from the width of the first phonon replica band of the A exciton, which was measured with the ISP-51 spectrograph.

The oscillograms of the blue luminescence of CdS at $\lambda = 4900$ Å and of the green edge luminescence at $\lambda = 5120$ Å are shown in Figs. 2b and 2c. The luminescence oscillograms obtained were analyzed taking account of the time resolution limit of the apparatus. The duration of the ruby laser pulses, measured with the FÉK-15 photocell, was not more than 0.3 nsec. However, this value was equal to the resolution time limit of the apparatus. In fact, the duration of the ruby laser pulses was only $\sim 10^{-11}$ sec, as found in the measurements involving pulse matching in a medium with two-photon absorption.[6] Thus, a laser pulse could be regarded as a δ function since its duration was much shorter than the resolution time of the apparatus.

It is known (see, for example,[9]) that a signal F(t) at the output of a linear system, with an impulse response h(t) and subjected to an input signal f(t), can be written as follows

$$F(t)=\int_0^t f(t')h(t-t')dt' \qquad (1)$$

The impulse response h(t) is the response of the system to an input which can be described by a δ-function.

The impulse response of the photomultiplier ÉLU-F7, which was used to measure the duration of the blue and green luminescence pulses emitted by a CdS crystal, was determined by applying a picosecond ruby laser pulse directly to its photocathode (Fig. 2d). The oscillogram of the signal obtained from the ÉLU-F7 is shown in Fig. 2e. The decay time of this signal has a "half-width" $\Delta t = 3.3$ nsec. If we assume that the impulse response of the ÉLU-F7 photomultiplier is the exponential function $\exp(-\beta t)$, we find that $\beta = (\ln 2)/\Delta t = 0.21$. The input function is also exponential, $\exp(-\alpha t)$, and it describes the time dependence of the intensity of the luminescence of the CdS. The time constant $\tau = 1/\alpha$ is the decay time which we want to measure.[1)] Substituting the functions $f(t) = \exp(-\alpha t)$ and $h(t) = \exp(-\beta t)$ in Eq. (1), we find that integration gives

$$F(t)=(\beta-\alpha)^{-1}(e^{-\alpha t}-e^{-\beta t}). \qquad (2)$$

A function of this type describes the shape of the blue luminescence pulse whose oscillogram is shown in Fig. 2b. The half-width of the pulse, described by the function F(t) of Eq. (2), is given by the difference of the roots of the equation

$$e^{-\alpha t}-e^{-\beta t}=\tfrac{1}{2}(e^{-\alpha t_m}-e^{-\beta t_m}), \qquad (3)$$

where $t_m = (\beta - \alpha)^{-1} \ln(\beta/\alpha)$ is the coordinate of the maximum of the function F(t) given by Eq. (2). We shall substitute $\beta = 0.21$ in Eq. (3) and solve this equation for various values of the parameter α, selecting a pulse half-width which will give the best agreement with the experimental value of the half-width. We thus find that the difference between the roots of Eq. (3) for $\alpha = 0.8$ is 6.3 nsec whereas the experimental value of the pulse half-width is 6 nsec. Thus, we may assume that $\alpha = 0.8$. This value corresponds to the decay time of the first phonon replica band of the A exciton given by $\tau = 1/\alpha = 1.3$ nsec. We note that the coordinate of the maximum of the function (2) for $\beta = 0.21$ and $\alpha = 0.8$ is 2.3 nsec, which agrees with the experimental value of the coordinate of the maximum of the blue luminescence pulse. The decay time of the green edge luminescence, deduced from the oscillogram in Fig. 2c, is 10 nsec.

It is interesting to note that the decay time of the first phonon replica line of the free excitons in Cd(SeS) was determined in[10] by excitation with a helium-neon laser. This decay time was $\sim 10^{-9}$ sec, which is very close to our results for CdS.

If we assume that the decay of the first phonon replica band of the A exciton in CdS is related to the reduction in the concentration of excitons as a result of their dissociation in collisions with phonons, we find that the exciton lifetime is given by the expression[11]

$$\tau=\frac{(2\pi\hbar^2)^{3/2}}{3^{1/2}\mu(kT)^2}\frac{1}{\sigma_{eh}}\exp(E_{ex}/kT), \qquad (4)$$

where μ is the reduced mass of an exciton; $E_{ex} = 0.028$ eV is the binding energy of an exciton; σ_{eh} is the average value of the effective cross section for binding an electron-hole pair into an exciton due to interaction with a phonon. It is shown in[11] that σ_{eh} is practically independent of the temperature. If we substitute $\tau = 1.3$ nsec into Eq. (4), we find that the value of σ_{eh} for CdS at $T = 77°K$ is 2.6×10^{-14} cm^2. This value is reasonable since the corresponding cross sections σ_{eh} for Ge and Cu_2O are $\sim 10^{-13}$ cm^2.[12]

The problem of the nature of the decay of the first phonon replica band of the A exciton in CdS is still unsolved and further studies are needed, including, in particular, an investigation of the temperature dependence of the decay time of this band. However, it is clear that the use of picosecond laser pulses in investigations of relaxation processes in solids is a very promising method and it can give some new results.

1)The parameters α and β are given in units of 10^9 sec^{-1}.

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