RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 28, NUMBER 10 15 NOVEMBER 1983

Study of dynamics of exciton polaritons by time-resolved luminescence

Farid Askary* and Peter Y. Yu
Department of Physics, University of California, Berkeley, California 97420
(Received 26 August 1983)

We present a simple two-branch polariton-model calculation which explains satisfactorily the experimental time-resolved luminescence spectra in CdS as a function of temperature.

Interaction between radiation and dipole-allowed excitons in solids results in coupled propagating modes known as exciton polaritons.[1] Exciton polaritons are important in understanding the optical properties of many semiconductors at low temperatures and their properties are still being investigated extensively.[2] In this Rapid Communication we present for the first time a theory which accounts for the complex time dependence of the luminescence spectra in CdS. The role of the polariton "bottleneck" first proposed by Toyozawa[3] in the thermalization of polaritons has been elucidated.

Figure 1 shows schematically the dispersion curves of an exciton polariton and that of an uncoupled transverse exciton and photon. The energies of the transverse and longitudinal excitons at zero wave vector have been denoted by E_T and E_L, respectively. The splitting between E_L and E_T depends on the oscillator strength of the exciton. Two notable features of the polariton dispersion relevant to this work are the presence of two branches (known as the upper and lower branches) and the absence of a low-energy limit in the lower polariton branch. Because of the latter, polaritons in the lower branch cannot attain thermal equilibrium since there are always lower-energy states for them to relax down to. However, Toyozawa[3] pointed out that polaritons have a bottleneck in their relaxation due to the sharp drop in the density of states below the "knee" in the dispersion curve (the cross-hatched area in Fig. 1). Polaritons can accumulate in this bottleneck and it has been shown that the main peak in polariton emission curves is associated with this bottleneck.[4]

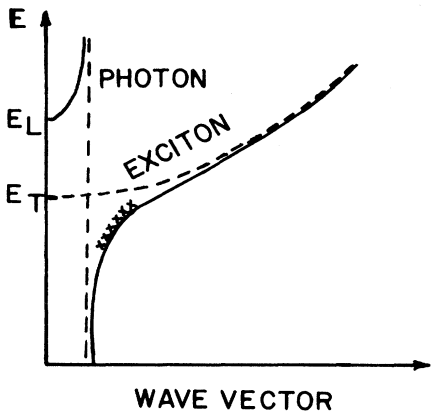

FIG. 1. Schematic polariton dispersion curve (solid lines) showing the location of the bottleneck (cross-hatched area). The dispersion curves of the uncoupled photon and exciton are shown as broken curves.

In principle, this polariton bottleneck can be located by measuring the polariton lifetime as a function of energy. Heim and Weisner[5] (hitherto referred to as HW) performed such an experiment on CdS. But instead of finding a peak in the polariton lifetime at some polariton energy, they reported that the polariton lifetime reached a *plateau* below E_T. Their results are reproduced in Fig. 2. HW concluded that their results are consistent with the existence of a polariton bottleneck in CdS but offered no quantitative explanations for their results.

Recently we have developed a simple two-branch polariton model including an additional boundary condition to explain quantitatively the polariton luminescence spectra of many semiconductors including CdS.[4] Using this model we have calculated the rate of decay of polaritons as a function of energy. We find a well-defined bottleneck in the polariton decay as predicted by Toyozawa.[3] In order to reconcile our calculation with the experimental results of HW we have reexamined the experimental time-resolved polariton luminescence (PL) in CdS.

The experimental setup we use is basically similar to those of HW and will be described in more detail elsewhere.[6] The ~150-psec-long pulses of an actively mode-locked Ar^+ laser (laser wavelength = 4579 Å) are used to excite PL from a high-quality CdS platelet cooled to liquid-He temperature. The PL emitted by the sample is first analyzed by a Spex double monochromator and then detect-

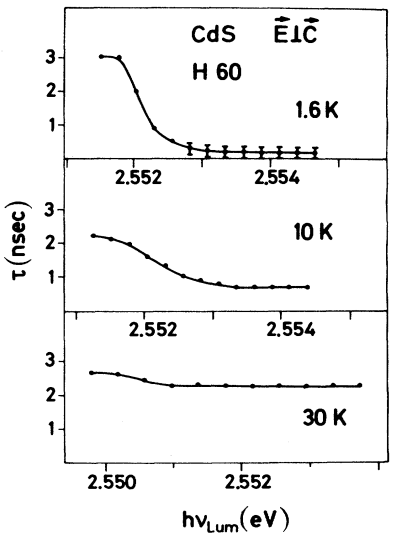

FIG. 2. Polariton decay times reported by HW for three different temperatures (reproduced from Ref. 5).

ed by a time-delayed coincidence photon counting system. The full width at half maximum of our system response in $\lesssim 0.5$ nsec and by deconvolution decay times of PL as short as 0.1 nsec can be determined. Figure 3 shows two typical PL decay curves of CdS we obtained at 6 K. It is clear that these decay curves are not exactly exponential. HW (Ref. 5) have also observed such nonexponential decays but they have used the $1/e$ decay time to determine their polariton lifetime τ_{ex}. We find that in most cases the PL decay curves can be fitted rather well by a sum of two exponential functions:

$$f(t)=\alpha_1 e^{-t/\tau_1}+\alpha_2 e^{-t/\tau_2} ,$$

where τ_2 will denote the faster decay time. The broken curves in Fig. 3 are obtained by convoluting $f(t)$ with the instrument response using τ_1, τ_2 and α_1/α_2 as adjustable parameters. The resultant values of τ_1, τ_2 and $\tau_1\alpha_1/\tau_2\alpha_2$ are plotted in Fig. 4. The quantity $\tau_1\alpha_1/\tau_2\alpha_2$ measures the relative contribution of the slow and fast components to the total time-integrated PL intensity. So by fitting the decay curves to a single exponential function, HW obtained a τ_{ex} dominated by the higher-intensity component. For polariton energy $E \gtrsim E_L$, τ_{ex} will be determined by the fast component (τ_2), while for $E \lesssim E_T$, τ_{ex} will switch over to the slower decay time τ_1. Thus we conclude that our actual PL decay curves must be similar to those obtained by HW although we have interpreted these decay curves differently.

To understand the nonexponential PL decay curves and the meaning of τ_1 and τ_2 we measured, we have utilized our model to compute numerically the polariton population as a function of time and energy.

Our model[4] is basically an extension of the one-branch model proposed by Sumi.[7] The important distinction between Sumi's model and ours is that we have included

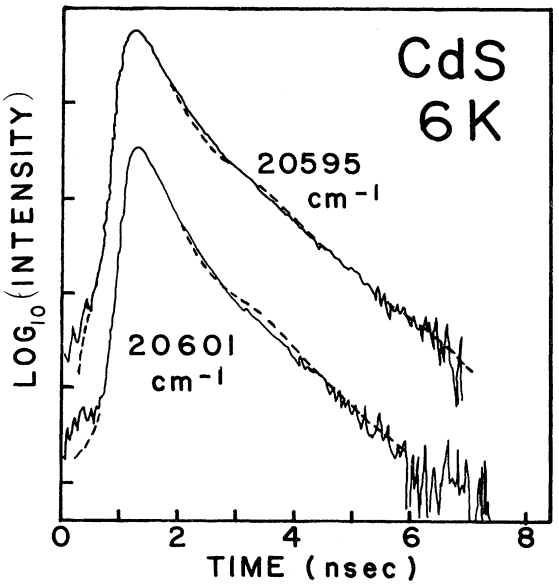

FIG. 3. Typical CdS polariton luminescence decay curves obtained at 6 K at two different polariton frequencies. The broken curves are fits to the experimental (solid) curves by convoluting the instrument response function with a sum of two exponential functions $f(t)$ as described in the text.

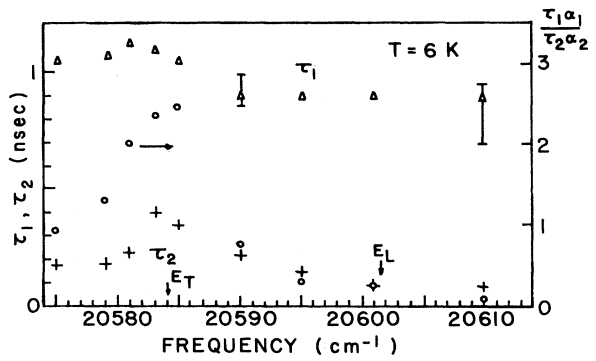

FIG. 4. The slow (τ_1) and fast (τ_2) decay times obtained from the CdS luminescence decay curves at 6 K. The open circles represent the relative contribution of slow and fast components to the total intensity. The frequencies of the longitudinal and transverse exciton have been indicated by arrows.

the upper polariton branch and therefore our model requires an additional boundary condition.[8] We have recently shown that Pekar's additional boundary condition[9] reproduced the time-integrated PL spectra of CdS very well. Assuming the excitation source to be a delta-function pulse in both time and energy, we obtain the time-dependent polariton distribution functions by solving two coupled Boltzmann equations of the form[4]

$$\frac{d\rho_i(E)}{dt}=\left[\frac{\partial\rho_i(E)}{\partial t}\right]_{\text{in}}-\left[\frac{\partial\rho_i(E)}{\partial t}\right]_{\text{out}} , \tag{1}$$

where i stands for either l or u and ρ_l and ρ_u are, respectively, the distribution functions of the lower and upper polariton branches. $(\partial\rho_i/\partial t)_{\text{in}}$ and $(\partial\rho_i/\partial t)_{\text{out}}$ are, respectively, the rate of generation and the rate of decay of polaritons. For simplicity, the polariton distribution is assumed to be homogeneous both in momentum space and in real space within a slab of thickness L. The polariton dispersion curves are also assumed to be isotropic in momentum space so that ρ_i depends on energy only. $(\partial\rho_i/\partial t)_{\text{in}}$ includes direct optical excitation [$\propto \delta(E-E_{ex})$, where $E_{ex} >> E_L$] and scattering in from other polariton states via acoustic phonons. $(\partial\rho_i/\partial t)_{\text{out}}$ includes radiative decay, out scattering by acoustic phonons, and trapping by impurities. The material parameters used in the calculation are those of CdS and can be found in Ref. 4. The computed time-dependent polariton populations are plotted on a semilogarithmic scale in Fig. 5 for three different temperatures. There are no adjustable parameters other than the impurity trapping rate which has been fixed at 3×10^8 sec^{-1} to correspond to the maximum τ_{ex} of ~ 3 nsec observed by HW.

We note that at $T=0$ K [Fig. 5(a)] the polariton populations decay exponentially in time. From these decay curves we determine the polariton lifetime as a function of energy. These are plotted as triangles in Fig. 6(a). For comparison we also compute the reciprocal of the polariton decay rates, γ^{-1}, and plot these as the solid line. It is interesting that γ^{-1} indicates a bottleneck at 20 588 cm^{-1} while the theoretical polariton lifetime shows a plateau as observed by HW at 1.6 K. The two results are actually consistent with each other. The explanation is that when several polariton states are coupled together, as they are in this case by phonon scatter-

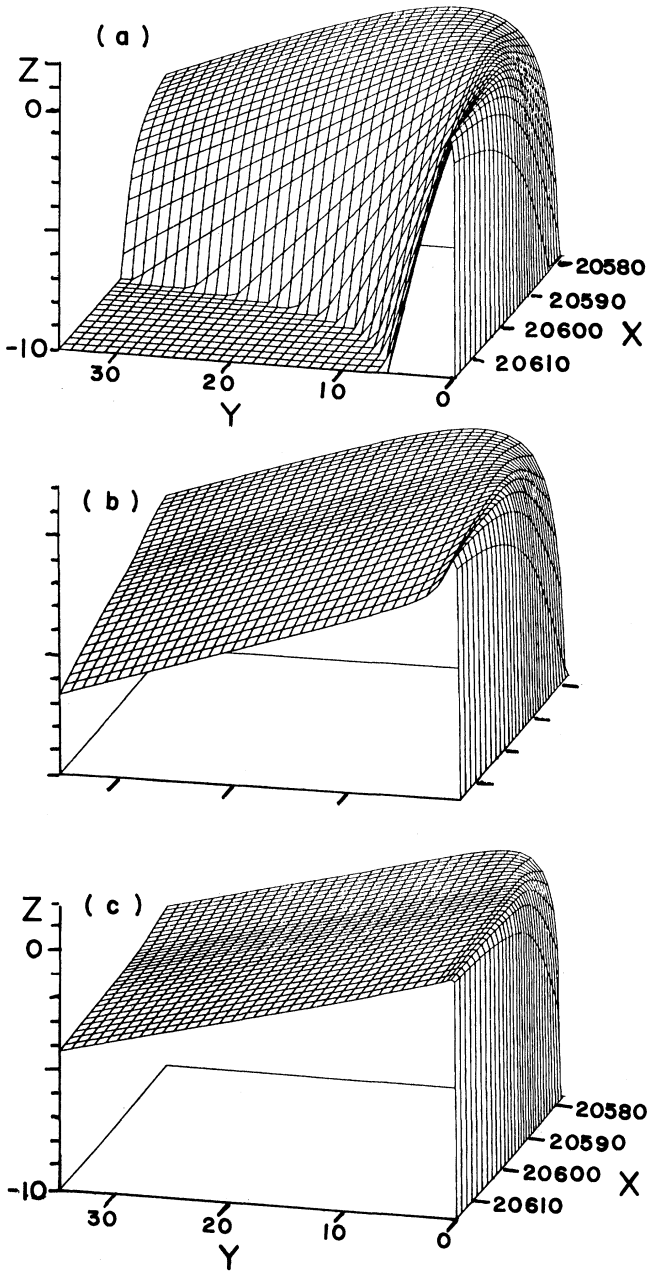

FIG. 5. Computed CdS luminescence decay curves at three temperatures: (a) 0 K, (b) 6 K, and (c) 25 K. The three axes X, Y, and Z represent, respectively, frequency (cm^{-1}), time (nsec), and the logarithm (base 10) of the intensity. The impurity trapping rate R is equal to 3×10^8 sec^{-1}.

ing, the lifetime of a particular polariton state is not necessarily given by γ^{-1}. For example, suppose a polariton state α decays at a rate γ_α but is populated almost instantaneously by another polariton state β with lifetime τ_β. If $\tau_\beta > \gamma_\alpha^{-1}$ then the population in α can be shown to depend on time as

$$(\tau_\beta - \gamma_\alpha^{-1})^{-1}(e^{-t/\tau_\beta} - e^{-t\gamma_\alpha})$$

(Ref. 6). For large enough values of t the decay in the population of α will be dominated by τ_β while only the rise time of the population in α depends on γ_α. This explains why polaritons below the bottleneck which are populated by relaxation of polaritons at the bottleneck have the same lifetime as polaritons at the bottleneck but show a finite rise time.

Next we turn our attention to the $T = 25$ K curves in Fig. 5(c). In this case the polariton decay curves are again exponential but the polariton lifetimes determined from these curves are constant and independent of energy as shown in Fig. 6(c). As pointed out by HW this indicates that polaritons at this temperature have reached a quasithermal equilibrium due to the fast acoustic-phonon scattering rate which now dominates γ.

Finally, for $0 < T < 25$ K the theoretical polariton decay curves in Fig. 5(b) are nonexponential for $E \gtrsim E_T$ in agreement with our experimental results at 6 K. Furthermore, the computed curves appear to contain two exponentially decaying functions. By fitting these curves with a sum of two exponentials we obtain the two decay-time constants shown as triangles and crosses in Fig. 6(b). Note that for Fig. 6(b) the impurity trapping rate has been increased to 9×10^8 sec^{-1} to correspond to the shorter polariton lifetime of ~ 1 nsec in our CdS sample. Qualitatively, Fig. 6(b) reproduces our results in Fig. 4 except for the magnitude of the fast decay time τ_2. The experimental values of τ_2 are smaller than the theoretical values because we have neglected the piezoelectric electron-acoustic phonon interaction.[10] By examining the theoretical decay curves we can now

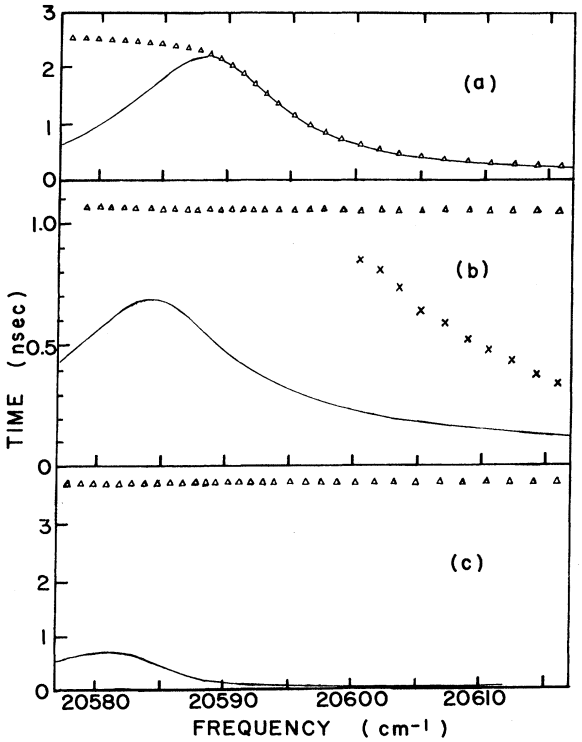

FIG. 6. The slow (triangles) and fast (crosses) decay time constants determined from the theoretical decay curves in (a) and (c). The results in (b) have been obtained from theoretical curves where R is equal to 8×10^8 sec^{-1}. In all three cases the solid curves represent the reciprocal of the polariton total decay rate γ^{-1}.

understand the meaning of τ_1 and τ_2. Immediately after excitation the population of polaritons with $E \gtrsim E_L$ builds up. They then relax via emission of acoustic phonons. *The fast decay time τ_2 is associated with the relaxation time of these nonequilibrium polariton populations.* The same relaxation processes start to populate the bottleneck region whose population shows a rise time of several nanoseconds. As polaritons accumulate in the bottleneck, they begin to scatter back up into the higher energy states by absorption of acoustic phonons. This "feedback" of polaritons from the bottleneck region slows down the decay of polaritons with energy $E > E_T$. If the polariton lifetime at the bottleneck is long compared with the phonon scattering time, eventually the entire polariton population will reach a quasithermal equilibrium and will decay with the same time constant τ_1. *Thus τ_1 represents the lifetime of the polariton population after attaining quasithermal equilibrium.* Such biexponential time decays have also recently been observed in Cu_2O due to thermalization between the orthoexcitons and paraexcitons.[11] With this picture it is clear that the $T = 0$ K decay curves cannot have a τ_1 since there cannot be quasithermal equilibrium without phonon absorption. On the other hand, for $T \gtrsim 25$ K, τ_2 becomes so short that quasithermal equilibrium among polaritons is almost instantaneous.

In conclusion, we have computed the time-dependent polariton population of CdS as a function of energy and temperature. These results are in good agreement with experimental time-resolved polariton luminescence data.

ACKNOWLEDGMENTS

This research is supported by the National Science Foundation through Grant No. DMR-79-19463. We are grateful to Y. Petroff and H. Cummins for providing us with CdS samples.

---

*Present address: Advanced Micro-Devices, Sunnyvale, CA 94086.

[1]J. J. Hopfield, Phys. Rev. 112, 1555 (1958).

[2]See articles in *Excitons,* edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982).

[3]Y. Toyozawa, Prog. Theor. Phys. Suppl. 12, 111 (1959).

[4]F. Askary and P. Y. Yu, Solid State Commun. 47, 241 (1983).

[5]U. Heim and P. Wiesner, Phys. Rev. Lett. 30, 1205 (1973); P. Wiesner and U. Heim, Phys. Rev. 11, 3071 (1975).

[6]F. Askary and P. Y. Yu (unpublished).

[7]H. Sumi, J. Phys. Soc. Jpn. 41, 526 (1976).

[8]See P. Halevi and G. Hernandez-Cocoletzi, Phys. Rev. Lett. 48, 1500 (1982), and references therein.

[9]S. I. Pekar, Zh. Eksp. Teor. Fiz. 33, 1022 (1957) [Sov. Phys. JETP 6, 785 (1958)]; 34, 1176 (1958) [7, 813 (1958)].

[10]G. D. Mahan and J. J. Hopfield, Phys. Rev. Lett. 12, 241 (1964).

[11]J. S. Weiner, N. Caswell, P. Y. Yu, and A. Mysyrowicz, Solid State Commun. 46, 105 (1983).