PHYSICAL REVIEW B VOLUME 57, NUMBER 7 15 FEBRUARY 1998-I

Time-resolved luminescence of exciton polaritons in PbI_2

Takayuki Makino
Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-01, Japan

Masayuki Watanabe and Tetsusuke Hayashi
Department of Fundamental Sciences, Faculty of Integrated Human Studies, Kyoto University, Kyoto 606-01, Japan

Masaaki Ashida
Department of Physics, Kyoto University, Kyoto 606-01, Japan

(Received 8 September 1997)

Exciton-polariton luminescence in PbI_2 single crystals is investigated at 5 K using picosecond time-resolved spectroscopy. Decay curves of the luminescence of exciton polaritons are compared with those of the optical phonon sideband. The temporal behaviors are consistently analyzed by taking into account the diffusive motion of polaritons, and the decay-time constants are obtained as a function of the luminescence photon energy. The decay time changes from 50 ps around the longitudinal exciton energy up to 140 ps at the energy a little below the transverse exciton one. The change is ascribed to intraband relaxation of polaritons toward the bottleneck region. [S0163-1829(98)03108-7]

An exciton polariton (EP) is a coupled mode between an exciton and a photon, and thus the radiative recombination of an exciton is regarded as a combined process of arrival of a polariton to the sample surface and subsequent conversion into a photon.[1,2] Pioneering works on the time-resolved luminescence of EP were performed in CdS and ZnTe.[3–5] The decay curves were fitted with two exponential functions and were interpreted to be due to the luminescence of hot and quasithermalized EP. In these cases the transport and the inhomogeneous distribution of EP inside the crystal were not considered. On the contrary, there are experimental reports on CuCl and solid Xe in which the decay curves yield nonexponential behavior.[6–8] In the experiment using thin platelet ($\simeq 10\ \mu$m) of CuCl crystals, an instantaneous response having a short decay time of about 10 ps was observed and explained by the coherent propagation of EP between front and rear surfaces.[6,7] On the other hand, the decay curves of EP luminescence in solid Xe with a thickness of ~1 mm were analyzed by taking into account the diffusive motion of EP.[8] The difference in these decay behaviors of EP probably resulted from the difference in the sample thickness as well as in the mean-free path of the coherent propagation of EP. In order to distinguish the contributions of the spatial propagation and the energy relaxation of EP on the luminescence decay, it may be useful to compare the decay behavior of EP luminescence with that of the phonon sideband. The temporal response of the phonon sideband directly reflects the lifetime of EP, since it is due to the EP scattered into the transparent region.

In the present paper, we report on the temporal response of EP luminescence in $2H$-PbI_2 single crystals. It is found that the decay curves of zero-phonon band of EP luminescence in PbI_2 are not represented simply by one or two exponential functions, while those of the phonon sideband yield single exponential decay. The decay curves of the former are analyzed by assuming one-dimensional diffusion of EP from the illuminated surface into the crystal. The derived decay-time constants are consistent with those deduced from the 2LO-phonon sideband. The temporal evolution of the lineshape of the sideband reveals the intraband relaxation of EP with acoustic phonon emission.

The PbI_2 single crystals with the thickness of ~1 mm were cooled down to 5 K in a liquid-helium cryostat. Incident light pulses were supplied from the second harmonics of a mode-locked Ti:Al_2O_3 laser pumped with a 10 W Ar^+ laser. The photon energy was tuned to 3.14 eV that corresponds to the band-to-band transition region of PbI_2. The pulse duration and the spectral width were about 2 ps and 1 meV, respectively, and the repetition rate was 82 MHz. The power of excitation was between 2 kW/cm^2 and 4 MW/cm^2. Luminescence from the illuminated surface of the sample was led into a single monochromator and detected with a rapid response photomultiplier or a charge coupled device detector, both attached to the monochromator. Time response of the luminescence was recorded by a time-correlated single-photon counting method. Overall time resolution of the system is about 10 ps and the spectral resolution is less than 1.2 A.

Figure 1 shows a time-integrated luminescence spectrum of PbI_2 at 5 K. The excitation intensity is 2 kW/cm^2. The bands denoted by FE, FE-A_{1g}, and FE-2LO are the zero-phonon luminescence of EP, its A_{1g}- and 2LO-phonon sidebands, respectively. The band marked ''I'' at 2.492 eV is the luminescence due to an impurity-bound exciton. The positions of transverse and longitudinal exciton energies ($E_T = 2.4979$ eV and $E_L = 2.5059$ eV) determined from reflection spectra are shown by lines.[9] The dotted curve shows the 2LO-phonon sideband obtained by subtracting the background intensity assumed as the broken curve.

Decay curves of FE are shown in Fig. 2(a). The curves measured at four photon energies are given by dots in the

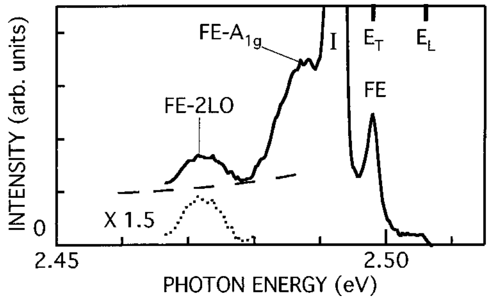

FIG. 1. Time-integrated luminescence spectrum of PbI_2 at 5 K measured under excitation in the band-to-band transition region. The resonant luminescence of exciton polaritons (FE) and its phonon sidebands (FE-A_{1g} and FE-2LO) are indicated by arrows. The marks E_T and E_L correspond to the transverse and longitudinal exciton energies, respectively.

logarithmic scale (three decades). Figure 2(b) shows those of FE-2LO band measured at the energies lower by 2LO-phonon energy ($2E_{\mathrm{LO}}$) from the corresponding ones of FE. Here, the decay curves in Fig. 2(b) were obtained by subtracting the background component of luminescence using the decay curve measured at the low energy end of the band (2.465 eV). The laser pulse measured directly is shown for comparison. The decay curves of FE-2LO band were almost approximated by single exponential decay except the weak and scattered signal after ~700 ps. The solid curves in Fig. 2(b) are the fitted ones obtained by convoluting the response of the laser pulses with single exponential decay functions [$\sim I_0 \exp(-t/\tau_0)$]. On the contrary, the decay curves of FE in Fig. 2(a) seemingly have shorter decay times than those of FE-2LO in Fig. 2(b). Since they are not reproduced in terms of single exponential decay, the decay curves of FE were fitted with appropriate functions formed by a series of exponential functions in order to obtain the true decay curves in which the effect of the instrumental response is removed. The results of the fitting are shown by solid curves in Fig. 2(a).

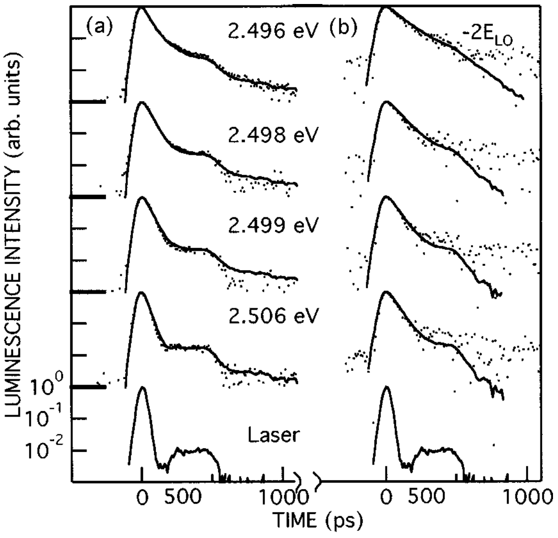

FIG. 2. Decay curves (●) of FE (a) and FE-2LO (b) bands measured at various photon energies. Solid curves are the fitted ones with the assumed decay functions (see text). The curves indicated by "laser" show the instrumental response.

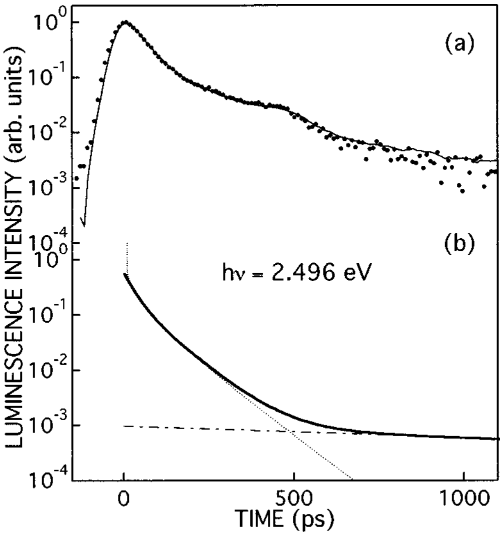

FIG. 3. (a) Decay curve of FE measured at 2.496 eV (●) and the fitted curve as in Fig. 2(a). (b) The solid curve shows the corresponding decay function obtained by removing the instrumental response. The dotted and dash-dotted curves show the results of fitting based on the first and second terms of Eq. (1), respectively.

Figure 3(a) shows the observed decay curve (●) and the fitted one (—) at the photon energy of 2.496 eV that are the same as the top of Fig. 2(a). The true decay curve obtained by removing the instrumental response is shown by the solid curve in Fig. 3(b). This decay curve seems to consist of a nonexponential decay component in the shorter time region below ~700 ps and a weak component with a slow decay. The dash-dotted curve in Fig. 3(b) shows an exponential decay presenting the slow component. The time constant of the slow component was not determined accurately, ranging around 1~2 ns, because of the very weak intensity. The origin of this component is not clear, and we neglect it at present.

Ikehara and Itoh[6] and Akiyama *et al.*[7] reported that the FE luminescence in a thin platelet (2~10 μm) of CuCl has a very short decay component with the time constant of about 10 ps. This pulse-like component was interpreted to be due to the coherent propagation of EP followed by the radiative escape from the crystal surface. The mean-free path of the propagation was longer than ~20 μm. Such a short decay component is not found in the present case. This is probably because the EP's suffer many steps of scattering until they arrive at the front surface of the very thick ($\simeq$1 mm) crystal. The short mean-free path of EP might also prevent the rapid propagation. In order to analyze the nonexponential decay shown in Fig. 3(b), we adopt the diffusion model of EP.[10] In the diffusion model, the time evolution of luminescence intensity is expressed in the first term of the following equation:

$$I(t) \propto I_0 (Dt)^{-d/2} \exp(-t/\tau_0) + I_1 \exp(-t/\tau_1), \qquad (1)$$

where d is the dimension in which the diffusion takes place, D, the diffusion coefficient, and τ_0 and τ_1, the decay-time constants, respectively. The second term in Eq. (1), single exponential decay, corresponds to the weak and slow com-

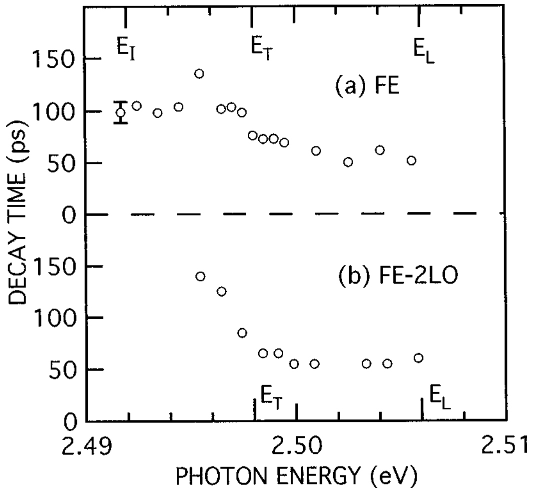

FIG. 4. Decay-time constant plotted against the luminescence photon energy for FE (a) and FE-2LO (b) bands. The marks E_T, E_L, and E_I correspond to the transverse, longitudinal, and bound exciton energies, respectively.

ponent shown in Fig. 3(b). Immediately after the photoexcitation at the band-to-band transition energy, EP's may be distributed within the region of the penetration depth of excitation light, and a part of them contribute to the luminescence. The luminescence intensity decreases not only by the intrinsic decay time τ_0 but also by the reduction in the density due to the diffusion inside the crystal. The solid curve in Fig. 3(b) can be fitted by the Eq. (1). The thin dotted curve corresponds to the first term. Here, we take $d=1$ (one-dimensional diffusion) because the diameter of excitation spot ($\simeq 100$ μm) on the sample surface is enough large compared with the penetration depth of excitation light. In fact, the accuracy of the fitting was somewhat low for choosing the higher dimension. Since the first term of Eq. (1) obviously diverges around $t=0$, the fitting is not valid around $t=0$. The fittings were satisfactory for all cases of various luminescence energies of EP in the time region after $t \simeq 40$ ps.

We thus determined the decay-time constants (τ_0) of FE (zero-phonon) band at various luminescence photon energies by virtue of the diffusion model. The results are shown in Fig. 4(a). The time constant varies from 50 ps near the longitudinal exciton energy up to 140 ps at the energy a little below the transverse exciton one. The decay time of the bound exciton luminescence (“E_I”) is around 100 ps. As mentioned before, the decay curves of the phonon sideband can be approximated by single exponential functions. The decay-time constants for the FE-2LO band are shown in Fig. 4(b). Here, the scale of the photon energy is upshifted by the amount of $2E_{\mathrm{LO}}$. The decay-time constants of FE-2LO band are very close to those of the FE at each photon energy. Although the temporal behaviors of the two bands are seemingly different with each other as seen in Fig. 2, it is found that they are consistently interpreted if the diffusion of EP are taken into account for the behavior of the FE band. Since the luminescence of FE-2LO band is due to the EP scattered into the transparent region, its temporal behavior directly reflects the lifetime of EP. The decay-time constants were not affected by the excitation power up to 4 MW/cm^2.

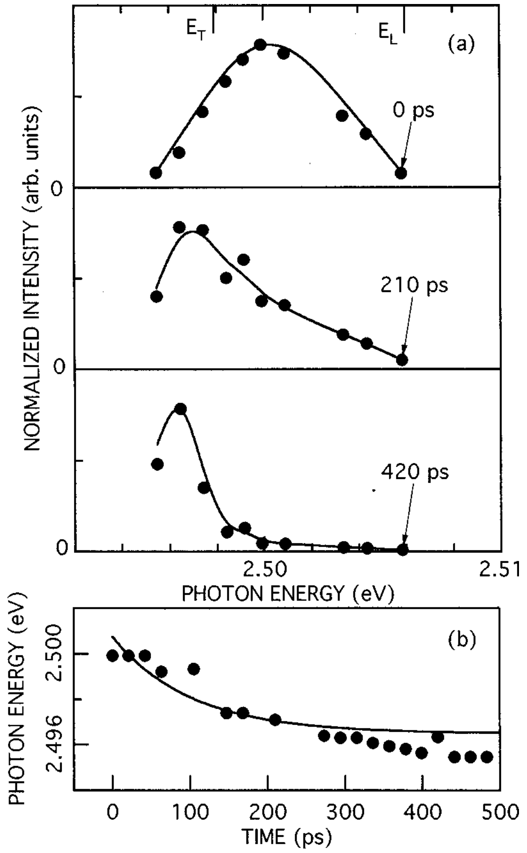

FIG. 5. (a) Time-resolved spectra of FE-2LO band. Delay times after the pulse excitation are indicated. (b) The peak energy of this band (added by $2E_{\mathrm{LO}}$) plotted as a function of time. A solid curve is the fitted result based on an exponential function.

We obtained time-resolved luminescence spectra from the decay curves measured at various photon energies by adjusting their time-integrated intensities with the steady-state spectrum. Figure 5(a) shows the spectra of FE-2LO band obtained for 0, 210, and 420 ps after the photoexcitation. Here, the photon energies are shifted by adding $2E_{\mathrm{LO}}$ to express the polariton energy. The intensities of these spectra are normalized at the respective peak. The solid curves are drawn only for a guide for the eye. We see the low-energy shift of the peak as well as the narrowing of the band with the lapse of time. This suggests that the change in the decay time with the luminescence energy shown in Fig. 4 arises from the polariton relaxation on the lower branch of the dispersion curve. The peak energies of the time-resolved spectra are plotted as a function of time in Fig. 5(b). The solid curve gives an exponential decrease in the peak energy with a time constant of 100 ps. This indicates that the polariton relaxation via acoustic phonon emission takes place in a time range of ~100 ps. The relaxation time is comparable with that in other semiconductors such as CdSe.[11] On the other hand, the spectrally integrated intensity of FE-2LO band is found to decrease with a time constant of 100 ps. This is comparable with the relaxation time and is fairly short compared with the lifetime of excitons in typical semiconductors (1–4 ns).[3,6,11]

In conclusion, the lifetimes of exciton polaritons in PbI_2 at various energies have been determined from the observed luminescence decay of the zero-phonon band by taking into account the diffusive motion of polaritons. These values are consistent with the decay times of FE-2LO sidebands. Intraband relaxation of polaritons on the dispersion curve with a time range of 100 ps is observed in spite of a very short lifetime of excitons.

This research was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

---

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

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

[3] P. Wiesner and U. Heim, Phys. Rev. B **11**, 3071 (1975).

[4] F. Askary and P. Y. Yu, Phys. Rev. B **31**, 6643 (1985).

[5] Y. Oka, K. Nakamura, and H. Fujisaki, Phys. Rev. Lett. **57**, 2856 (1986).

[6] T. Ikehara and T. Itoh, Phys. Rev. B **44**, 9283 (1991).

[7] H. Akiyama, T. Kuga, M. Matsuoka, and M. Kuwata-Gonokami, Phys. Rev. B **42**, 5621 (1990).

[8] D. Varding, I. Reimand, and G. Zimmerer, Phys. Status Solidi B **185**, 301 (1994).

[9] M. Watanabe and T. Hayashi, J. Phys. Soc. Jpn. **63**, 785 (1994).

[10] N. N. Zinov'ev *et al.*, Zh. Eksp. Teor. Fiz. **84**, 2153 (1983) [Sov. Phys. JETP **57**, 1254 (1983)].

[11] Y. Masumoto and S. Shionoya, Phys. Rev. B **30**, 1076 (1984).