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Biexciton lifetime in CuCl observed with weak picosecond pulse excitation

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We have observed at 4.2 K the emission of biexcitons in CuCl (the M emission) created via two-photon absorption under a weak excitation condition by means of a high-repetition-rate (82-MHz) picosecond-tunable uv light source obtained by sum frequency generation. The spectral shape and the time response are measured. The results are quite different from the previous work measured under stronger excitation conditions and show that the lifetime of the biexcitons is short, about 30 ps, and they experience no momentum relaxation at this temperature.

In some semiconductors two excitons interact attractively and form a bound state known as a biexciton.[1] They can be created via collisions of high-density excitons. They can also be created directly by two-photon absorption. The latter process is quite efficient and called giant two-photon absorption. Biexcitons annihilate and emit radiation leaving excitons. This is called M emission and its spectral shape and temporal behavior are important for studies of biexcitons. We report in this paper a careful study of M emission in CuCl at 4.2 K under a weak excitation condition in the picosecond time domain. We have obtained quite different results from the previous ones in the spectral shape and lifetime.

About ten years ago, M emission in CuCl was intensively studied both spectrally and temporally stemming from the interest in Bose condensation of biexcitons and in the distinction between the luminescence and the resonant Raman scattering. The spectrum of M emission is known to consist of the following three components:[2] a sharp line, called the M line, coming from the emission of biexcitons which do not experience momentum relaxation after the direct excitation via two-photon absorption; a broadband, called the M band, attributed to the emission of distributed biexcitons with the Maxwell distribution; and a two-photon Raman line which overlaps with the M line under the exact resonance condition. In the previous time-resolved measurements[3,4] of M emission, a slow decay component (several hundred picoseconds[3]) and a fast one were observed. It was then concluded that these two components were luminescence and two-photon resonant Raman scattering, and the decay time of the slow component was the lifetime of the biexcitons.

But in these previous experiments it was not easy to know the elementary properties of biexcitons which were not affected by strong excitation effects. The experiments in the frequency domain were performed using nanosecond-pulse dye lasers pumped by a N_2 laser or an excimer laser. The long pulse duration easily caused the accumulation of excitons and/or biexcitons. Thus it was difficult to eliminate high-density-excitaion effects such as biexciton-biexciton scattering, biexciton-exciton scattering, biexciton formation by exciton-exciton collisions, and reabsorption of the M emission. The experiments in the time domain were carried out using picosecond-pulse lasers such as dye lasers pumped by the third harmonic of a pulsed mode-locked yttrium aluminum garnet (YAG) laser. Because of the low repetition rate and the low duty ratio in this case, a high peak power (0.4–1 MW) was necessary to obtain a sufficient signal-to-noise ratio, and this made the reduction of high-denisty-excitation effects difficult. For the investigation of relaxation processes in the excited states, experiments without strong excitation effects are very important in the first place; they are fundamental to the studies under various excitation conditions.

Recently, we have developed a picosecond-tunable uv light source with a high-repetition rate (82 MHz) by means of a sum frequency generation,[5] and applied it to a time-resolved spectroscopy of exciton luminescence.[6] We now prove that this light source enables us to observe M emission and measure the temporal response under about 10^{-5} times as weak excitation as before. Platelets of CuCl single crystals with thicknesses of 2.6 to 20 μm were immersed in liquid He in strain-free states. The excitation light having the pulse train of a peak power of 4 W and a pulse duration of 8 ps, and having the spectral width of 2 Å, was focused on the sample with a spot size of 50 μm in diameter. The experimental setup was the same as that of the previous work[5,6] except that the time resolution was improved by limiting the used area of the grating of a monochromator.

Figure 1 shows the time-integrated forward (a) and backward (b) emission spectra from CuCl under the excitation at the two-photon resonance of biexciton, 3.186 eV. The sharp lines are observed at 3.164 and 3.170 eV, and they are designated as M_L and M_T lines (the subscripts L and T mean the longitudinal and the transverse exciton remaining after each process). When we change the exci-

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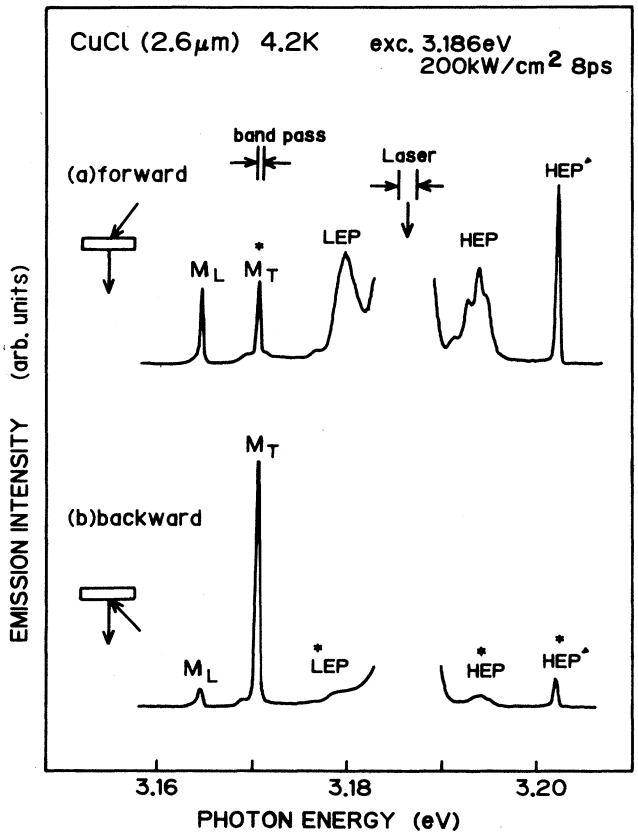

FIG. 1. Time-integrated forward (a) and backward (b) emission spectra of CuCl at 4.2 K. The excitation light energy is tuned to 3.186 eV, and the two-photon resonance of biexciton. The lines M_T, M_L, HEP, LEP, and HEP' correspond to various radiative decay processes of biexcitons. The peaks marked by an asterisk are the emissions detected via reflection from the rear surface.

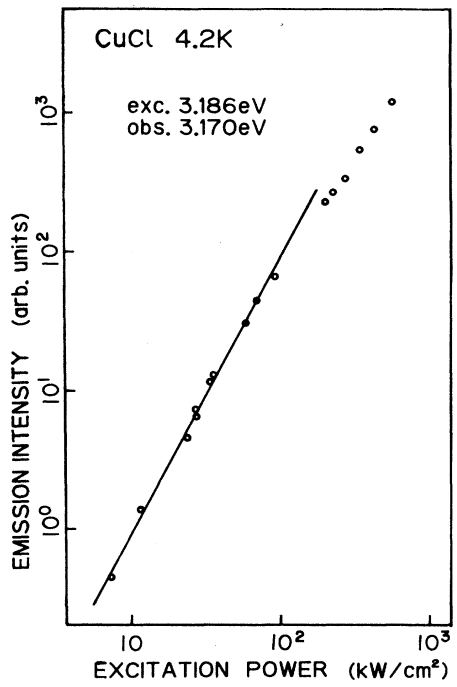

FIG. 2. Intensity of the M_T line vs the excitation power. The dots represent the measured data. The solid line shows a quadratic dependence. The excitation power is the peak power calculated from the average power assuming that the light pulses have a rectangular shape in time and a uniform circular shape in space.

tation photon energy around 3.186 eV, the sharp lines decrease in intensity but do not shift, and neither off-resonant Raman lines nor M bands are observed. The observed widths of the M_T and M_L lines are limited by the bandpass of the monochromator. This sharpness means that the M lines are "cold" emissions[2] of the biexcitons; the biexcitons decay radiatively before they are distributed within the momentum space by interacting with each other or with phonons. Figure 2 is the plot of the M_T line intensities against the excitation power. The M_T line intensity shows quadratic dependence, which gives evidence that there are no higher-order nonlinear effects in these excitation power levels. The peaks denoted[7] LEP and HEP on both sides of the laser line in Fig. 1 are due to the radiative decay of biexcitons into two photons. The sharp line at 3.202 eV denoted HEP' is the emission of the excitons remaining after the M_T process. The intensities and the energies of these lines are determined by the geometrical selection rule.[7] The peaks marked by an asterisk are the emissions detected via reflection from the rear surface.

We have measured the temporal responses of these peaks with a synchroscan streak camera behind the monochromator. Figure 3 shows the response of the M_T line in the backward-scattering geometry. Also shown is the profile of the laser. Its width indicates the temporal resolution of our system. The intensity of the M_T line decreases exponentially with a decay-time constant of about 30 ps. This is also the case with the other three lines: M_L, LEP, and HEP. The intensities of these four lines are proportional to the biexciton population, so that the decay time, 30 ps, is the lifetime of biexcitons. The dependence of the decay time on the excitation power is examined within the region shown in Fig. 2, but no pronounced change is observed. Therefore our measurements are free from high-density-excitation effects, and the biexciton lifetime is 30 ps in the weak excitation limit.

The previous time-resolved experiments reported a slower decay time or component of M emission[3,4] under stronger excitation conditions. Considering the newly measured lifetime of the biexcitons, 30 ps, and that of the excitons, on the order of nanoseconds,[8] we may explain the previous results as follows. Under the strong excitation by a picosecond pulse a number of biexcitons are excited by two-photon absorption. In about 30 ps they decay to excitons radiatively and the excitons accumulate. They reabsorb the radiation of the M emissions or collide with each other to become biexcitons again. In this way, the excitation of the excitons to biexcitons and the decay of the biexcitons to excitons repeat until the excitons die off. Therefore the observed M emissions show slower decay.

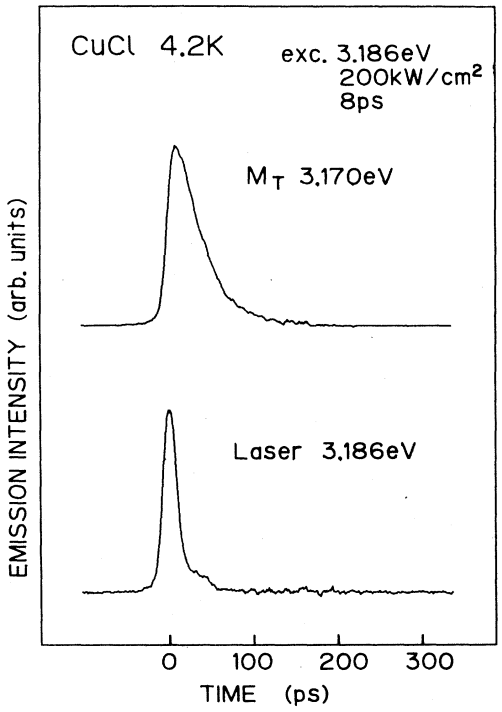

FIG. 3. Time trace of M_T line (above) and that of excitation light (below) measured in the backward-scattering geometry with the synchroscan streak camera. The pulse duration of the excitation light is 8 ps, the value measured by autocorrelation technique. The intensity of the M_T line decreases exponentially with a decay constant of about 30 ps.

We should note the fact that the M bands are missing and only the sharp M lines appear in Fig. 1. This is also true when the excitation intensity is increased to 1 MW/cm^2. This is evidence that the biexcitons do not distribute in the momentum space during their lifetime by collisions among them or with phonons at 4.2 K under the present excitation condition. It is known that the M bands appear under the excitation by nanosecond pulses of the same peak intensity.[9] If we use a nanosecond pulse, whose duration is much longer than the lifetime of the biexcitons and is comparable to that of the excitons, accumulation of excitons easily occurs, and they create biexcitons distributed in the momentum space giving the broad M bands. Therefore the distributed biexcitons observed in this case are not produced as the result of the collisions among them or with phonons but by the accumulated excitons. The absence of the M bands in our data indicates again that high-denisty excitaion is avoided.

Several authors[3,4] concluded that the luminescence and the resonant Raman scattering can be distinguished by two components in the time responses of the M lines, the fast one being the Raman scattering and the slow one being the luminescence. Our results are different. The decay curve of the M emissions is well fitted by single exponential curves and there is no special feature to distinguish the luminescence from the resonant Raman components.

Bose condensation of biexcitons is expected when one considers the biexcitons' boson nature and light translational mass.[10] About ten years ago, the observation of the condensation in CuCl was claimed in some papers,[11,12] which, however, induced a lot of refutations and discussions. The results of our new experiment deny a possibility of Bose condensation of biexcitons in CuCl. That is, the lifetime of the biexcitons is shorter than the phonon relaxation time and therefore the biexcitons die out before they cool to the condensed state giving excess kinetic energy to the lattice.

The time trace of the HEP' line on the other hand is quite different from those of the other four lines in Fig. 1. As shown in Fig. 4, in the forward-scattering geometry (a) it rises gradually from $t=0$, and falls rapidly at $t=T$, then again rises from $t=2T$, and falls at $t=3T$. In the backward case (b) it starts rising at $t=T$, and falls at $t=2T$. This extraordinary behavior can be interpreted by taking account of the polariton behavior of the excitons as follows. In a crystal the coupling of a photon and a transverse exciton composes an exciton polariton. It is well known that the polariton picture holds well for Z_3 excitons in CuCl.[1,5,6] The excitation light is converted into polaritons having the wave vector $\mathbf{k}_0$ at the surface. They pass through the sample with a very fast group velocity because of a large off-resonance and create biexcitons with the wave vector $2\mathbf{k}_0$. Because the biexcitons move much slower than the polaritons, spatial distribution of

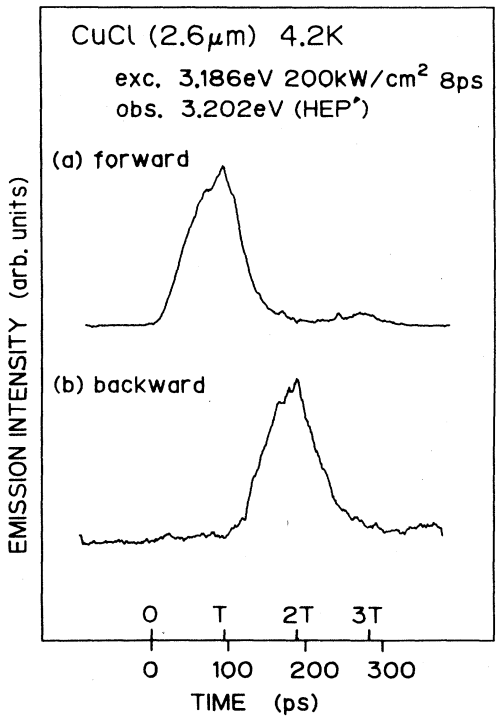

FIG. 4. Time traces of the HEP' line measured in the (a) forward- and the (b) backward-scattering geometry by the synchroscan streak camera. They reflect the spatial distribution of biexcitons, the biexciton lifetime and the group velocity of the HEP' exciton polariton. The time T in the figure is the traveling time of the polariton from one surface to the other.

biexcitons along the propagation direction is proportional to the square of the number of $\mathbf{k}_0$ polaritons at each point. The number decreases by two-photon absorption. In 30 ps the biexcitons emit $-\mathbf{k}_1$ polaritons by the M_T process and leave $2\mathbf{k}_0+\mathbf{k}_1$ polaritons with the spatial distribution determined by that of the biexcitons. When they come to the rear surface, a number of them are transmitted through it and are detected as the forward emission. The rest are reflected and reach the front surface. Some of them are emitted outside of the crystal and detected as the backward emission. The rest go back, and so forth. The time T is the traveling time[13] from one surface to the other with the group velocity at $2\mathbf{k}_0+\mathbf{k}_1$.

These time traces as well as the sharpness of the HEP' line in Fig. 1 show that the created polaritons do not relax into the "bottleneck" region by repeating acoustic-phonon scattering, but travel, keeping their initial wave vector. The result here is quite consistent with that of our recent work.[5,6] The fact that the wave vectors of the exciton-polariton state, the final state of the M_T emission, remain at $2\mathbf{k}_0+\mathbf{k}_1$ confirms that the wave vectors of the biexciton state, the intermediate state, are not diverged. As a whole, wave vectors are not disturbed by phonon scatterings, by biexciton-biexciton collisions, or by polariton-polariton collisions throughout the process.

In conclusion, we have observed the spectra and the time traces of the M emissions in CuCl free from the high-density-excitation effects using the weak and short excitation pulses from the high-repetition-rate, picosecond-uv light source. The lifetime of the biexcitons is found to be 30 ps, during which the momentum relaxation does not take place. This result is different from the previous ones with strong excitation. The discrepancy that the M bands and the slow components of the M emissions are present or absent is explained by the high-density-excitation effects. The spectral and the temporal behavior of the exciton-emission line also show that the intraband relaxation is absent in the polariton propagation.

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[1]For a review of the recent research on biexcitons, refer to M. Ueta, H. Kanzaki, K. Kobayashi, Y. Toyozawa, and E. Hanamura, *Excitonic Processes in Solids* (Springer-Verlag, Berlin, 1986).

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