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STUDIES OF EXCITON-POLARITON DYNAMICS BY LUMINESCENCE AND RAMAN SCATTERING IN ZnTe

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Abstract - Time characteristics of Raman-like 1LO and 2LO lines have been measured in ZnTe under the condition that the energy of the 1LO line is located at the polariton bottleneck. These lines have been found to decay much faster than polariton luminescence. It has also been found that the decay time of the polariton luminescence depends on the excitation intensity. The relation between the time behavior of the secondary emissions and the relaxation property of the excitonic polariton is discussed.

I - INTRODUCTION

Although several features of excitonic polaritons have been well clarified, direct information about their dynamical properties is quite scarce. The resonant second-order optical processes mediated by excitonic polaritons /1/ reflect the relaxations in the intermediate polariton states and are considered to give detailed information on the polariton dynamics. In the present paper, we report measurements of the time behavior of secondary radiation from resonantly excited ZnTe. Particularly, using a tunable dye laser for the excitation, we have compared the time characteristics between Raman-like lines and ordinary luminescence bands for the case where the exciting photon energy fulfills the energy of the transverse exciton with zero momentum $E_T$ by about one longitudinal-optical (LO) phonon energy $\omega_0$.

When a ZnTe crystal of high purity is excited with green or blue Ar laser light at low temperatures, Raman-like lines and ordinary luminescence bands are observed in the same energy region around the band-gap /2,3/. The energy positions of the Raman-like lines are separated from the laser line by multiples of the LO phonon energy $\omega_0 = 26$ meV. Therefore, these lines are considered to be due to the LO-phonon-assisted processes. These LO lines show resonance enhancement when the line position approaches $E_T$. When the exciting photon energy is varied above the band-gap, the energies of the LO lines change by the same amount, while the spectral shape and position of the ordinary luminescence remain almost unchanged. Above ~60 K, bound-exciton lines are not observed, and the ordinary luminescence near the fundamental absorption edge consists of two asymmetric broad bands. From the energy position and wavelength-dependence of the decay time, these bands are ascribed to luminescence due to excitonic polaritons distributed on the dispersion curves /3/.

Measurements of the time characteristics of the secondary emission intensity using...
the 514.5 nm pulses from a mode-locked Ar\(^+\) laser showed that, around 70 K, the lifetime of the lower-branch polariton is of the order of 100 ps below the knee of the polariton dispersion curve, and it shortens remarkably with increasing energy above the knee region /3/. Further, the Raman-like lines were found to decay within the time resolution of the measurement of \(\approx 10\) ps. In this case, the exciting photon energy \(\Omega_1\) is located about 1.5 \(\omega_0\) above \(E_T\). On the other hand, the case where \(\Omega_1 - \omega_0\) is a little lower than \(E_T\) is very interesting, because only the lower-branch polariton state which has a relatively long lifetime is available as the energy-conserving intermediate state at the energy of \(\Omega_1 - \omega_0\). We have studied the time characteristics of the Raman-like \(1\)LO and 2LO lines for this case of \(\Omega_1 = 2.390\) eV at 77 K (\(E_T = 2.366\) eV) in detail using a time-correlated single-photon counting method /4/.

II - EXPERIMENTAL PROCEDURE

The samples employed are undoped single crystals grown by the Bridgman method. They were immersed into liquid nitrogen and excited with a mode-locked Ar\(^+\) laser and a coumarin 535 dye laser synchronously pumped by the 488 nm line of a mode-locked Ar\(^+\) laser (Spectra Physics 171). The secondary emission from the cleaved sample surface was analyzed by a 0.85-m double monochromator (Spex 14018) and detected by a microchannel-plate photomultiplier (Hamamatsu Photonics R1564U). The time-correlated single-photon counting apparatus used has already been described in detail /4,5/.

Although the spread of the electron transit time in the photomultiplier employed was only about 50 ps /6/, the widths of the response curves of our system to the Ar and dye laser pulses were \(\approx 130\) and \(\approx 190\) ps, respectively. The time resolution of the measurement obtained by curve fitting was about 10 ps.

III - EXPERIMENTAL RESULTS

Figure 1(a) shows the secondary emission spectra of ZnTe excited with the 514.5 nm

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Fig. 1 - Secondary emission spectra (a), and time responses at the peak of the luminescence band (b), of ZnTe at 77 K excited with the 514.5 nm mode-locked laser pulses of various intensities.

The spot size of the exciting laser light on the sample was about 1 mm\(^2\), and the average light power is given in each figure. The spectra are normalized at the peak of the luminescence band.
Ar laser light of various intensities. The broad LP and UP bands are ascribed to the luminescence due to lower-branch and upper-branch polaritons, respectively. On the other hand, the narrow 2LO line is the Raman-like line associated with the emission of two LO phonons. In Fig. 1(a), the intensity ratio between the 2LO line and the polariton luminescence band depends on the excitation intensity. This is because the ordinary luminescence intensity increases superlinearly with the excitation intensity, while the dependence is almost linear for the Raman-like lines. The superlinear excitation-intensity dependence was observed even when the exciting photon energy was lower than $E_T$.

Figure 1(b) shows the decay characteristics of the polariton luminescence intensity under the excitation powers corresponding to Fig. 1(a). Luminescence at the polariton bottleneck decays within the time resolution of our measurement when the excitation intensity is sufficiently low, but its decay time increases with increasing excitation density and becomes about 60 ps at the excitation power of 10 mW. It has also been found that the superposition of the CW light on the exciting pulse lengthens the decay time of the polariton luminescence. These results are explained by the mechanism that the polariton damping rate decreases on account of the filling of the trapping centers when the excitation power is increased. Previously reported measurements of the time characteristics /3,7/ correspond to a relatively high excitation case of the present experiment.

Next, we compared the decay times of the Raman-like lines with that of the polariton luminescence under the condition that the 1LO line is located at the polariton bottleneck. The spectrum and the time responses of the secondary emissions excited

![Figure 2 - Secondary emission spectrum of ZnTe at 77 K excited with the 518.6 nm mode-locked laser light.](image)

![Figure 3 - Time responses for the secondary emission of ZnTe at 77 K excited with the 518.6 nm mode-locked laser light.](image)
at 2.390 eV are shown in Figs. 2 and 3, respectively. A relatively high excitation intensity was used in order to make the decay time of the polariton luminescence long enough to be resolved by our system. The decay time of the 2LO line intensity was determined by measuring the time behavior of the total secondary emission intensity at the wavelength of the 2LO line, i.e. the sum of the 2LO line and the broad luminescence band, and subtracting the time behavior of the broad luminescence component. As the latter behavior, we employed the average of the time dependence of the broad luminescence just above the 2LO line in energy and that just below the 2LO line. This procedure is justified because the energy dependence of the luminescence decay time as well as that of the emission intensity does not show any abrupt change around the energy of the 2LO line /3/.

As shown in Fig. 3(c), when the time behavior of the superposed luminescence is subtracted from that of the total secondary emission intensity at the energy of the 2LO line, the rest coincides with the response curve of our system to the exciting laser pulse within the experimental error. This indicates that the Raman-like 2LO line is emitted within the time resolution of our experiment of \( \sim 10 \) ps. The measurement for the 1LO line also gave the same result. On the other hand, as shown in Fig. 3(d), the polariton luminescence in the neighborhood of the 1LO line decays with a time constant of \( \sim 70 \) ps, which is apparently much longer than the decay times of the 1LO and 2LO lines.

IV - DISCUSSION

Recently, a calculation of the time-resolved secondary emission spectrum in an exciton-phonon system was reported by Aihara and Kotani /8/. These authors calculated the time behavior for the 2LO-phonon-assisted process and showed that the Raman-like component results not only from the pure Raman process associated with virtual intermediate states, but also from the hot luminescence process, in which the energy-conserving real intermediate states are concerned. Further, it was concluded that when the excitation pulse duration is shorter than the lifetime of the intermediate-state exciton at the energy of \( \Omega_1 - \omega_o \), the decay time of the Raman-like 2LO line is determined by the lifetime of this exciton, and accordingly this line should be regarded as hot luminescence. Basing on this consideration, Aihara and Kotani /8/ proposed to apply the method to measure the time behavior of the 2LO line for the determination of the exciton lifetime.

In the measurement previously performed on ZnTe around the liquid nitrogen temperature, however, the decay time of the Raman-like 2LO line under the 514.5 nm laser excitation was too short to be determined by the experimental system employed /3/. One might consider that the lifetime of the intermediate-state exciton at the energy of \( \Omega_1 - \omega_o \) is rather long in this case, because this exciton cannot decay by emitting an LO phonon. However, the energy dependence of the decay time of the polariton luminescence shows that the polariton with the energy \( \Omega_1 - \omega_o \) has a very short lifetime in this case, probably because of the fast scattering by phonons, nonradiative decay through crystal imperfections, and so on /3/. Therefore, it was not clarified by this experiment whether the time behavior of the Raman-like 2LO line reflects the lifetime of the energy-conserving intermediate state or not.

It should be rather easy to see if the decay time of the 2LO line is determined by the lifetime of the intermediate state having the energy of the 1LO line, when this line is located at the polariton bottleneck, since the polariton in this region is known to have a relatively long lifetime. In order to fulfill this condition, a tunable dye laser was employed in the present experiment. As mentioned in the preceding section, the decay time of the 2LO line was found to be sufficiently short in ZnTe, even when the intermediate-state polariton with the energy of \( \Omega_1 - \omega_o \) is located at the energy region where the polariton lifetime is long enough to be determined by our system.

The fact that the lifetime of the energy-conserving intermediate polariton state is not reflected on the time behavior of the 2LO line is interpreted in terms that the polariton (or exciton) state with the energy \( \Omega_1 - \omega_o \), which plays the dominant role as the intermediate state of the transition, acts as the virtual intermediate state
in the 2LO line emission process. This means that the phase memory is preserved for this state during the emission process of the 2LO line. In this case, the decay time of this line can be shorter than the lifetime of the energy-conserving intermediate state because of the interference effect \(^/9/\).

In the previous experiment \(/3/\), the decay time (<10 ps) of the 2LO line was found to be much shorter than the decay time of the luminescence around the 2LO line. In another experiment \(/10/\), all the 1LO, 2LO and 3LO lines were observed to decay within 10 ps, which is again much shorter than the decay times of the luminescence around these lines. The fast decay of the LO lines is not considered to imply that the polaritons really created at a given point on the dispersion curve are distributed around the nearby points within 10 ps. If this were the case, the luminescence decay time must be independent of the polariton energy, as long as the decay time is much longer than 10 ps. However, the fast decay of the 2LO line was observed even when this line was located at the region where the decay time of the polariton luminescence was relatively long and energy-dependent. Because the decay time of the 2LO line is much shorter than the lifetime of the polariton with the same energy, it is necessary to consider two kinds of polaritons. It may be possible to call them really and virtually created polaritons \(/10/\). As is clear from the interference analogy of Raman-luminescence problem \(/9/\), the secondary emission due to virtually created polariton can decay much faster than the lifetimes of the polaritons concerned.

In the case of polariton, since the intermediate states are present continuously in energy, the time behavior of the secondary emission via the virtual intermediate states is expected to follow that of the exciting pulse \(/7/\). Namely, in the present case, the secondary emission process of the Raman-like LO lines is considered to be as follows. The polariton wave packet created at the energy \(\Omega_1\) of the upper branch by the incident light pulse is scattered by one or two LO phonons and the polariton wave packets are generated around the energies of \(\Omega_1 - \omega_0\) and \(\Omega_1 - 2\omega_0\). They produce secondary emission pulses with almost the same duration as the incident light, because the phase relation among the polaritons (or excitons) with the energies around \(\Omega_1, \Omega_1 - \omega_0\) and \(\Omega_1 - 2\omega_0\) is preserved during the secondary emission process, and also because the LO-phonon scattering rate as well as the photon-polariton conversion rate is not very energy-sensitive for the polaritons concerned. This means that the 2LO line and also the 1LO line in our case should not be regarded as hot luminescence but as genuine Raman scattering. This result is consistent with those of the previous reports \(/3,9,10/\).

REFERENCES