Two-Photon Raman Scattering and High Excitation Luminescence in ZnTe

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Two-Photon-Raman Scattering (TPRS) and the luminescence of ZnTe are investigated when the samples are highly excited with a tunable narrow-band dye-laser. In luminescence, one observes emission bands due to the well-known inelastic exciton-exciton scattering at intermediate excitation intensities, and the recombination radiation of an electron-hole plasma (EHP) at the highest excitation levels. For the first time, TPRS is reported in ZnTe. From the change in the TPRS lines in magnetic fields up to 10T we deduce a diamagnetic shift of $1.2 \cdot 10^{-2}$ meV/T$^2$ of the free longitudinal exciton. This value is in good agreement with results obtained by other authors from reflection spectroscopy.

I. Introduction

If (direct gap) semiconductors are highly excited with photons of energy $\hbar \omega_{\text{exc}}$ equal to or larger than the free exciton energy $E_x$, the luminescence spectra generally yield information about excitonic interaction processes or electron-hole plasmas (EHP). For recent reviews of this subject see e.g., [1–3] and the literature cited therein. For $\hbar \omega_{\text{exc}} < E_x$, two-photon Raman scattering (TPRS) can be observed in high quality samples. The quantitative evaluation of these Raman spectra gives rather direct access to exciton- and polariton dispersion curves. See e.g. [3, 4] and the literature cited therein.

In this contribution, we present luminescence spectra caused by (1) inelastic exciton-exciton scattering and (2) by radiative recombination in an EHP. Furthermore, TPRS and its behaviour in a magnetic field are investigated.

II. Experimental Set-up

The excitation source is a N$_2$-laser pumped dye-laser (Lambda FL 2000 E) which gives pulses with a peak power of about 10 kW. The spectral width $\Delta \lambda$ is reduced by a grating, a telescope and a Perot-Fabry etalon to values of $\Delta \lambda \sim 0.02 \text{Å}$. Repetition rate and temporal halfwidth $\tau_L$ of the pulses are 30 Hz and 2 ns, respectively. The diameter $D$ of the excitation spot on the sample is varied between 100 μm and 500 μm. The excitation intensity $I_{\text{exc}}$ can be decreased at constant spot size by neutral density filters.
The geometrical arrangement for luminescence and TPRS measurements is shown in the inset of Fig. 1. Either cleaved or polished and etched surfaces of the high quality, melt-grown samples are used. The samples are immersed in liquid He pumped to 2 K. The sample cryostate is inserted in a superconducting coil which produces magnetic fields up to 10 T. The emission of the sample is dispersed by a 1.5 m spectrometer and detected by a SIT vidicon and an OMA-2 system. The dispersion is about 0.13 Å/channel = 0.06 meV/channel.

III. Experimental Results and Discussion

In the first part of this chapter, we deal with the luminescence, in the second part with TPRS.

1. Luminescence

In Fig. 1, typical luminescence spectra are shown for $\hbar\omega_{\text{exc}} \geq E_x$. At moderately high $I_{\text{exc}}$ (Fig. 1a) one observes at 2.375 eV and 2.3743 eV the emission lines of excitons bound to neutral acceptors [5, 6]. In a magnetic field the 2.375 eV line splits into at least three components. The splitting increases approximately linearly with $B$ and amounts to about 0.3 meV at $B = 10$ T. The luminescence intensity of the components decreases towards higher values of $\hbar\omega_{\text{num}}$ and the intensity ratios are consistent with a lattice temperature of 2 K. Some information about the magnetic field behaviour of bound excitons is also given e.g. in [6].

The dominant emission structure in Fig. 1a is the so-called P-luminescence band around 2.367 eV. This band has been identified as being due to inelastic exciton-exciton scattering [7, 8], because of its spectral position and the fine-structure ($P_2$ and $P_\infty$), observed under favourable conditions. In [9], the P-band has been attributed to the radiative recombination in an electron hole droplet. This assignment seems rather unlikely to us, since we observe at higher $I_{\text{exc}}$ a strongly stimulated emission band at lower wavelength (see Fig. 1b). We interpret the new emission band in Fig. 1b as due to the luminescence from an EHP for the following reasons:

- The emission appears at the highest $I_{\text{exc}}$ where the formation of an EHP is most likely.
- The emission band is strongly stimulated, as can be expected for the EHP recombination in semiconductors with a direct, dipole-allowed gap.
- The shape of the emission band is smooth without structure.

Though the most reliable information about an

<table>
<thead>
<tr>
<th>$E_x - \mu$</th>
<th>$\mu - E'_x$</th>
<th>$n_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>12 ± 2 meV</td>
<td>17 ± 4 meV</td>
</tr>
<tr>
<td>Theory [10]</td>
<td>3 meV</td>
<td>21.4 meV</td>
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</tbody>
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EHP in a direct gap semiconductor can be obtained from gain spectroscopy with the two-beam method (e.g. [2, 3]), the luminescence spectrum also allows approximate values of the relevant parameters to be deduced.

Its high energy edge coincides roughly with the chemical potential $\mu$ of the EHP, where the crossover from gain to absorption occurs ($\mu \sim 2.368$ eV ± 2 meV). Its low-energy side gives the reduced gap $E'_x$ ($E'_x \sim 2.350$ eV ± 2 meV). From Fig. 1b, we deduce the values given in Table 1, and from the difference $\mu - E'_x$ and the effective masses we calculate the plasma density $n_p$, assuming that the plasma temperature is not too high ($T_p < 20$ K).

Concerning the values for $n_p$ and $\mu - E'_x$, the agreement between experiment and theory is good. The theory underestimates the binding energy of the plasma, however, as is often the case for direct semiconductors [2, 3].

In the moment, there is no indication that the EHP reaches a liquid-like state or even forms droplets as claimed in [9]. No Landau-level structure can be detected in the EHP-recombination band in fields up to 10 T, though the sum of electron and hole cyclotron energies $\hbar(c_e + c_h)$ exceeds 10 meV at 10 T. This is consistent with strong temporal and/or spatial fluctuations of the plasma density $n_p$: the reduced gap $E'_x$ is a monotonously decreasing function of $n_p$. Fluctuations in $n_p$ will result in a superposition of Landau-ladders with different starting points $E'_x(n_p) + \frac{1}{2} \hbar(c_e + c_h)$ and possible structures are consequently averaged out. For a discussion of this point see e.g. [3, 12].

2. Two-Photon Raman Scattering (TPRS)

Figure 2 shows emission spectra obtained with intermediate high excitation for $\hbar\omega_{\text{exc}} < E_x$. Apart from the P-band and the bound exciton lines at 2.375 eV and 2.3743 eV already discussed in III.1, one observes another bound exciton line at 2.3685 eV and an emission called the M band at 2.379 eV, which is believed to be due to the radiative decay of biexcitons [13].

In addition, a rather narrow emission line is found (FWHM ~ 0.5 meV) which shifts with $\hbar\omega_{\text{exc}}$. 