EFFECTS OF EXCITONIC MOLECULES ON EMISSION AND TRANSMISSION SPECTRA OF CdS SINGLE CRYSTALS

J. Voigt and F. Henneberger

Sektion Physik der Humboldt-Universität
zu Berlin, Bereich Halbleiteroptik

ABSTRACT

Based on new results of transmission and emission experiments on CdS single crystals in a very extended range of excitation intensities at 1.8 K, we discuss the annihilation and formation of excitonic molecules in a model involving A_{Γ_6}-excitons and A_{Γ_5}-polaritons. It is shown that the presented results as well as those by Saito and Shionoya can be consistently explained in this model. A theoretical foundation of the model and a way to calculate emission and absorption spectra due to excitonic molecules are presented.

I. INTRODUCTION

In CdS single crystals, depending on the experimental conditions used, two excitonic molecule (EM) emission lines are reported in the literature differing in line shape and energetic position.[1,2] Saito and Shionoya[1] found, under 100 kW pulsed laser excitation, a new line in the emission spectrum of CdS at 2.546~2.544 eV whose position and half-width depend on the excitation intensity. We reported[2] a characteristic emission spectrum with a main peak at 2.5492 eV, appearing in very thin high-quality CdS single crystals at low temperature, under intense stationary excitation by a high pressure mercury lamp. To explain both lines on the basis of EM-annihilation, we extended the model[1] used up to that time for this process by including the polariton character of A_{Γ_5} ground state excitons. Additionally, A_{Γ_6} ground state excitons are taken into consideration. In this model, the line reported by Saito and Shionoya (M_s) is attributed to transitions at EM of wave vectors $k_M > k_{photon}$, whereas the line reported by us (M_1) corresponds to transitions at $k_M \approx 0$. In the following, this "polariton"-model of EM-

annihilation was supported by results of transmission experiments.[3] Besides an absorption peak (M_1) at E_1 = 2.5491 eV, which we attributed to the direct formation of EM by optical absorption reverse to the EM-annihilation involving A_{Γ_6}-excitons, we found a second (smaller) peak (M_2) at E_2 = 2.5471 eV, which we ascribed to EM-formation from excitons of the energy E_L = 2.5547 eV (*i.e.* exciton-like A_{Γ_5}-polaritons of the upper branch as well as longitudinal excitons). Recently, Müller *et al.*[4] observed a correlation between (M_S) and (M_1) EM-emission lines at different excitation intensities and concluded also that (M_S) and (M_1) were due to EM having $k_M > k_{photon}$ and $k_M \approx 0$, respectively.

In this paper we report new experimental results of transmission and emission experiments on CdS single crystals in a very extended range of excitation intensities at 1.8 K, which confirm the proposed "polariton"-model of EM-annihilation in detail, and, in particular, explain the correlation between the different EM-lines (M_1), (M_2) and (M_S). Furthermore, a theoretical foundation of the model is given and formulas are derived for evaluating emission and transmission spectra.

II. EXPERIMENTAL

The experimental arrangement used is described in detail in ref. (5). The CdS single crystals investigated were grown from the vapour phase with thickness ranging from 5×10^{-5} to 5×10^{-4} cm. The samples were carefully prepared and mounted in such a way that no internal strains occurred with decreasing crystal temperature. The measuring temperature was 1.8 K (samples immersed in the liquid helium bath).

III. RESULTS

At stationary excitation three characteristic emission lines lying energetically below the free exciton emission are observed (Fig.1, curve 6): The EM-line (M_1) at E_1 = 2.549 eV (halfwidth H≈1.5 meV) investigated by us in detail in ref. (2), the line (M_2) at E_2 = 2.5469 eV (H≈

0.5 meV), observed so far only in transmission,[3] and the line at E_{I_2} = 2.5460 eV ($H \approx 0.5$ meV), whose intensity strongly increases with increasing crystal thickness, whereas the ratio of intensities of the lines (M_1) and (M_2) is nearly constant in all crystals.

At lowest laser excitation*) only the lines (M_1) ($H \approx 1.4$ meV) and

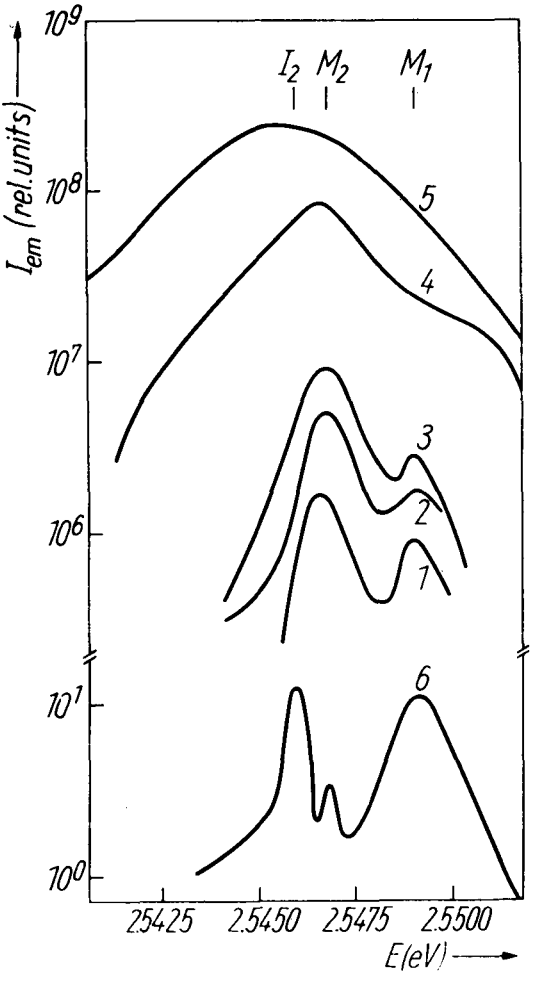

Fig.1. Spectral dependence of the emission at different laser intensities ((1) 1.3% I_0, (2) 2.5% I_0, (3) 5.4% I_0, (4) 12% I_0, (5) 37% I_0) and at stationary excitation (6) $\vec{E} \perp \vec{C}$, T = 1.8 K.

*) The lowest laser intensities used in our experiments to resolve (M_1) and (M_2) are more than two magnitudes smaller than the lowest one in the experiment of Saito and Shionoya.[1]

M_2 (H ≈ 1.4 meV) appear (Fig. 1, curves 1 and 2). The essential difference in comparison to the spectra at stationary excitation consists in the fact that (M_2) is the dominant line. With increasing laser excitation, (M_2) grows more strongly than (M_1) and this is accompanied by some broadening (Fig. 1, curve 3). At still higher excitations, (M_2) is transformed to the line (M_S) (H ≈ 5 meV) whose energetic position shifts to low energy side with increasing excitation intensity (Fig. 1, curves 4 and 5). The line (M_1) contributes to a high energy tail of (M_S), as seen from a shoulder (Fig. 1, curve 4) appearing at not too high excitation intensities.

The transmission spectrum of the crystal investigated in emission is given in Fig. 2. Besides the well pronounced spike at the longitu-

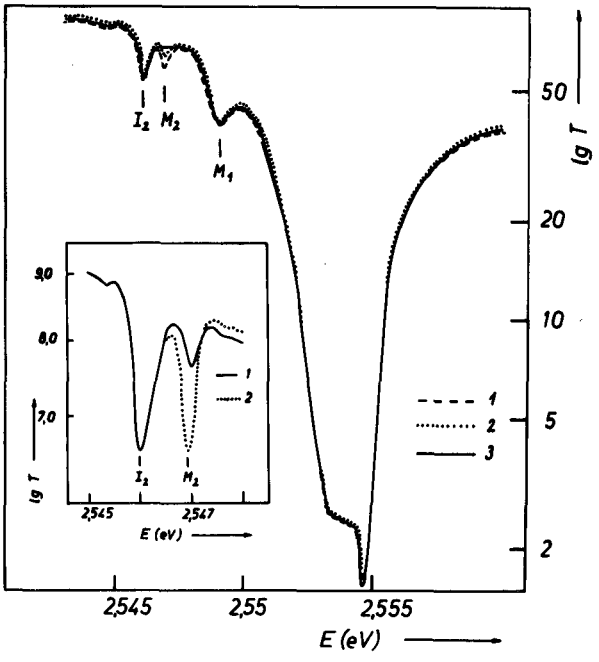

Fig.2. Spectral dependence of the transmission at different incident light intensities ((1) I_0, (2) 22% I , (3) 5.6% I_0). Insert: (1) without additional light, (2) HBO 500 λ < 400 nm.

dinal energy E_L = 2.5546 eV all structures found in the emission (M_1), (M_2) and I_2 are reproduced in the transmission showing a very good agreement with respect to the energetic positions as well as the half-widths. With increasing intensity of the incident light a remarkable

change of the transmission spectrum is only found in the line (M_2) (the spectra of Fig. 2 are normalized to constant incident intensity), whose intensity increases. At low intensities (M_2) cannot longer be detected in transmission. On the other hand, a strong additional excitation with $\lambda < \lambda_{ex}$ results in a strong enhancement of the line M_2 (see insert in Fig. 2).

IV. DISCUSSION

4.1 Qualitative Interpretation

The experimental results can be consistently explained in the model for EM-annihilation proposed by us in ref. (2) which involves both, A_{Γ_6}-excitons and A_{Γ_5}-polaritons (Fig. 3). The line at E_{I_2} = 2.5460 eV is attributed to the known I_2 bound exciton emission[5] because of its dependence on sample thickness and its absence even at the lowest laser excitation intensity. The lines (M_1),

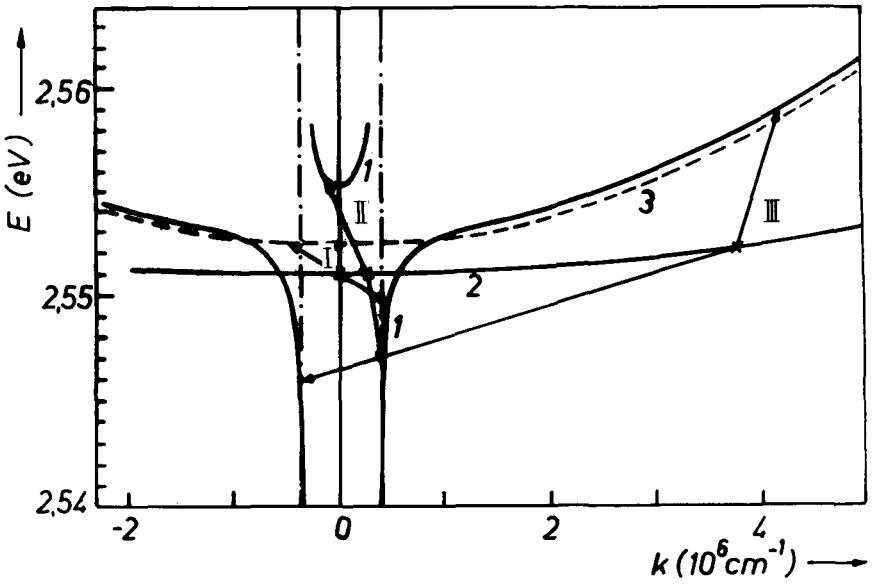

Fig.3. Dispersion curves of the A_{Γ_5}-polariton (1), EM (2), and A_{Γ_6}-exciton (3).

(M_2) and (M_S) are interpreted as being due to EM-annihilation. Without consideration of A_{Γ_6}-excitons, due to the splitting of the dispersion

curves of A_{Γ_5}-polaritons two EM-emission lines are expected in the model given in Fig. 3 (transitions II and III) leaving exciton-like polaritons in the upper and lower polariton branch, respectively. The transition II is only allowed (due to energy momentum conservation) for a very small range of k_M-values where the dispersion of EM can be neglected, resulting in a sharp emission line, whereas the main part of transition III is given by EM's with $k_M > k_{photon}$. The transition I designates the radiative recombination of EM's leaving a A_{Γ_6}-exciton. There are two reasons from which we conclude that (M_1) is correlated to the transition I rather than to the transition III. Firstly, (M_1) does not shift to low energy side with increasing laser intensity as one expects for transition III due to the heating of the EM gas. Secondly, the difference $E_1 - E_2 = 2.2$ meV is greater than the longitudinal-transverse splitting of the A_{Γ_5}-exciton, $E_{\Gamma_{5L}} - E_{\Gamma_{5T}} = 1.9$ meV, determined from the transmission measurement of high precision.[6] But excellent agreement is obtained by setting $E_1 - E_2 = E_{\Gamma_{5T}} - E_{\Gamma_6}$ and taking into account the electron-hole exchange splitting; $E_{\Gamma_{5T}} - E_{\Gamma_6} \lesssim 0.4$ meV.

The line (M_2) is attributed to the transition II, from its energetic position and halfwidth. The line (M_S) includes all transitions I, II and III, but the dominant transition is the transition III due to the distribution of EM in the band with a maximum at $k_M > k_{photon}$. On the other hand, at stationary excitation, where the temperature of the EM gas coincides with the lattice temperature, a narrow distribution of EM near $k_M = 0$ exists, resulting in dominant lines (M_1) and (M_2). Therefore, the redistribution of EM in the band with increasing laser intensity causes the observed changes in the emission spectra.

The results of transmission measurements, carried out at "normal" intensities, show that the processes I and II can take place also in reverse direction. But the intensity dependence one expects[7] is only verified for the line (M_2). The behaviour of the line (M_1) can be explained, taking into consideration the different relaxation times of

the processes involved.

4.2 Theoretical Remarks

In earlier theoretical calculations[7,8] of the emission and absorption spectrum of EM, the polariton-effect of excitons as final and initial states of the considered transitions has been neglected. Therefore, the theoretical results are only applicable to EM and excitons of translational momentum large in comparison to that of photons. However, our experimental results show that EM and excitons of small momentum play a dominant role. Thus, the extension of the conventional models of EM-annihilation and formation is necessary.

To include polariton-effects for these processes we start from the model Hamiltonian H given by Hanamura.[8] (The interaction between EM's is neglected because its smallness at the considered excitation densities). Following Hopfield[9] we transform H into the polariton representation, introducing annihilation and creation operators a^{+}_{ik}, a_{ik} of polaritons at energy $E_i(k)$; i = 1,2, as linear combinations of the corresponding exciton and photon operators. Then H can be written as

$$H = H_M + H_{POL} + H_{M\text{-}POL}, \tag{1}$$

where H_M and H_{POL} describe non-interacting EM and exciton-polariton systems, respectively. The interaction between both systems is given by $H_{M\text{-}POL}$, its explicit form is written as

$$H_{M\text{-}POL} = \sum_{i,j=1}^{2} \sum_{\vec{k},\vec{q},\vec{q}'} C_{i1}(\vec{q})F(\vec{k})C_{i2}(\vec{q})\delta(\vec{k}-\vec{q}-\vec{q}')a^{+}_{i\vec{q}}a^{+}_{j\vec{q}'}C_{\vec{k}} + \text{h.c.} \tag{2}$$

($C^{+}_{\vec{k}}$ - creation operator of EM of momentum $\vec{k}$). The coupling constant $F(\vec{k})$ is proportional to the oscillator strength calculated by Gogolin and Rashba,[7] $C_{ij(\vec{q})}$ is the transformation matrix tabulated in ref.(9). From eq.(1) the used transitions scheme (Fig. 3) can be justified immediately. In this picture the EM-annihilation (leaving a photon and an exciton) and the reverse absorption process is replaced by the decay of

EM into two polaritons and the reverse fusion process due to the interaction (2). Treating H_{M-POL} as perturbation, the optical spectra of EM can be calculated in the framework of first order perturbation theory. Basing on this concept we have derived formulas for emission and absorption spectra of EM, which cannot be presented in this short paper (because their analytical form is very lengthy). Generally, they depend on

1. The ordinary oscillator strength of the optical transition[7] and, additionally, the polariton transformation coefficients[9] which characterize the exciton- and photon-like character of polaritons.
2. The density of states of the interband energy $E_M(k) - E_i(k)$ (instead of $E_M(k) - E_{ex}(k)$).[7,8]
3. The occupation numbers of EM (emission) and polariton states (absorption).

To make a comparison of experimental and theoretical results it is necessary to carry out numerical computations using the occupation numbers of EM and polaritons as fitting parameters. This will be reported in a forthcoming paper.[10]

ACKNOWLEDGEMENTS

We are greatly indebted to Prof. E. Gutsche for critical remarks on the manuscript. We thank Mr. J. Puls for making the transmission experiments.

REFERENCES

1) H. Saito and S. Shionoya, *Proc. Internat. Conf. Luminescence, Leningrad* (1972) ed. F. Williams (Plenum, N. Y., 1973) p.104.
2) J. Voigt and G. Mauersberger, Phys. Stat. sol. (b) 60 (1973) 679.
3) J. Voigt and 1. Rückmann, Phys. Stat. sol. (b) 61 (1974) K85.
4) G. O. Müller *Proc. 12th Internat. Conf. Phys. Semicond., Stuttgart* (1974) ed. M. H. Pilkuhn (Teubner, Stuttgart, 1974) p.123.

5) J. Voigt, F. Mir, and G. Kehrberg, Phys. Stat. sol. (b) 70 (1975) 625.

6) J. Voigt, Phys. Stat. sol. (b) 64 (1974) 549.

7) A. A. Gogolin and E. I. Rashba, Zh, eksper. theor. Fiz. 17 (1973) 69.

8) E. Hanamura, *Proc. Internat. Conf. Luminescence, Leningrad* (1972) ed. by F. Williams (Plenum Press, N.Y., 1973) p.121.

9) J. J. Hopfield, Phys. Rev. 112 (1958) 1555.

10) F. Henneberger and J. Voigt, to be published.