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Influence of Exciton-Exciton Interaction on the Edge Emission in CdSe Single Crystals

I. CHUDÁČEK
Department of Solid State Physics, Faculty of Mathematics and Physics,
Charles University, Prague
J. VAITKUS, R. BALTRAMEJUNAS and V. NJUNKA
Department of Semiconductors, Kapsukas' State University, Vilnius

I. Introduction

Recently have appeared many papers devoted to the mutual interaction of excitons. Related phenomena have been explained by the following mechanisms:

(1) Generation of the exciton molecule called the biexciton [1], [2], [3], [4]

(2) Origination of the "exciton fluid" [5]

(3) Overlap of the exciton and conduction energy bands [6], [7]

(4) Interaction between excitons and between excitons and free electrons [8], [9].

Obviously the above mentioned mechanisms 1–4 will be unequally pronounced according to the kind of excitation and the typ of semiconductor. These mechanisms were the most frequently studied on semiconductors which have been excited with the electron beam at the low temperatures. It was discovered the stimulated emission due to the high concentration of excitons occured even at relatively high temperatures of about 400°K [6], [8], [10].

The following reasons compelled us to have chosen the CdSe for the present study:

(1) The structure of excitons is well known in this material [11]

(2) The high levels of excitation give rise to the stimulated emission [10], [12], [13]

(3) The exciton-exciton interaction at low temperatures was found in CdSe [14]

Independently on the various kinds of excitation different authors are claiming the different laws governing the edge luminescence. Having partially started from our previous paper [15] we tried in this work to examine the edge emission.

2. Experimental technique

The single crystals of CdSe were grown both from the gaseous phase and from the melt. The biphotonic processes were created in the crystals by means of the excitation with the neodymium one mode laser. The approximate intensity was about

10^7 W/cm^2 and the duration of the pulse shorter than 50 n sec. The samples were placed in the cryostat enabling the temperature control in the range from 77 to 300°K.

The emission spectrum of the edge luminescence was registered with ISP 51 spectrograph on a photographic plate. The blackening curve of the photographic material was obtained with the attenuated light from the ruby laser.

The measuring of the dependence luminescence intensity on the intensity of excitation was carried on in the same experimental arrangement. The hight from the laser was detected with a coaxial photoelement. The luminescence was measured either with a coaxial photoelement or with a photomultiplier. The both pulses were traced on the cathode tube of the sampling oscilloscope. When evaluating the emission spectra the reabsorption of the luminescence we took into account similarly as in [18]. We used the absorption spectra published in [16] and [17] which were measured on the single crystals of CdSe of the same origin.

3. Results

The dependence of the maximum of emission spectrum on temperature is given in Fig. 1. On Fig. 2 are shown the emission spectra obtained at two different temperatures with no respect to reabsorption and the corrected ones respectively. For five different samples we got the same temperature dependence when the reabsorption was assumed. If we had not included the correction on reabsorption we got the different temperature dependences for different samples even within an experimental
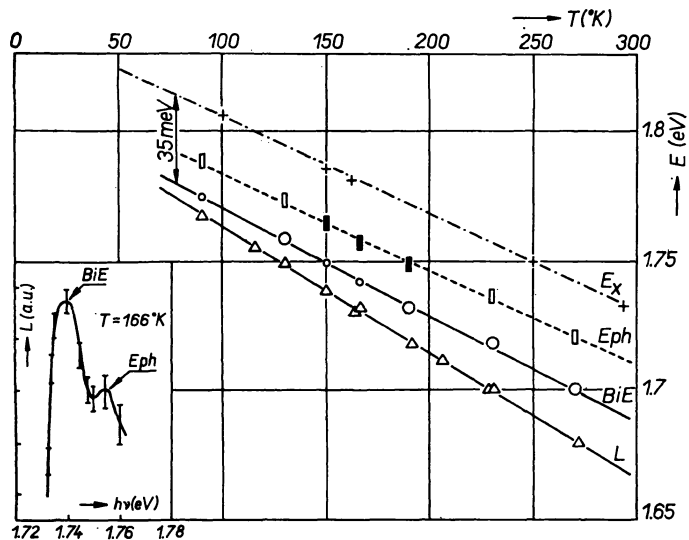

Fig. 1. Temperature dependence of the maximum of different emission spectra. L — non corrected emission on reabsorption, BiE, Eph — biexcitonic and excitonic emission maximum, F_x — temperature dependence of the energy level of A exciton. At left side the corrected spectrum of luminescence at 166 °K

error. The analysis in the short wave side behind the maximum was possible only for a few samples. This is in connection to the fact the reabsorption in the short wave side of the main absorption is due to the existence of a nonluminescent thin layer on the surface of the sample [19]. In cases we were able to analyze the region behind the main maximum the second emission band had appeared. Its temperature depen-
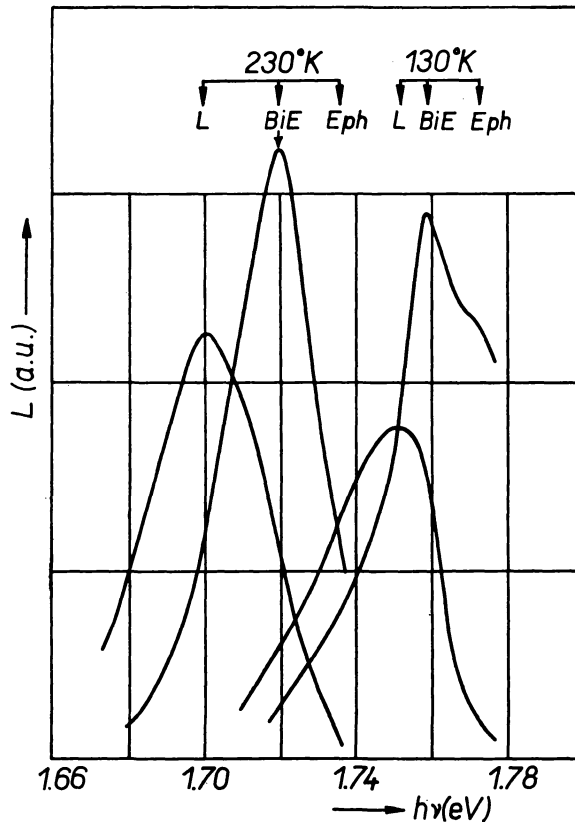

Fig. 2. The spectra of uncorrected (L) and corrected (BiE, Eph) edge emission at the temperature of 230°K 130°K

dence is shown on Fig. 1. Having compared our own results with those in [10] we concluded that the measured emission corresponded to the radiative annihilation of an exciton accompanied with the emission of longitudinal phonon.

At the temperature of 77°K the main emission band is shifted from the A level of exciton of 35 meV. This shift increases with the temperature. The temperature dependence of the position of the maximum as obtained in the experiment is possible to approximate in the given temperature range by the relation

$$h\nu_{\max} = E^* - a\,T$$

where $E^* = 1.812 \pm 0.002$ eV and $a = 4.15 \cdot 10^{-4}$ eV/°K. The coefficient a is analogius to that of the temperature dependence either of the energy gap or the basic level A of the exciton. This one in CdSe equals to $3.76 \cdot 10^{-4}$ eV/°K [16].

4. Interpretation of Results

The analysis of the recombination kinetics at high intensities of excitation anables us to show [8], [20] that observed kinetic dependences is possible to explain by the creation and annihilation of exciton molecules. This applies mainly to the feature of the intensity dependence both of luminescence and photoconductivity. Both exciton-electron and Auger's recombination can occure.

The radiative annihilation of a biexciton gives rise to a pair of excitons, one of them recombinates radiatively. The relevant experimental observable is the short wave side of the emission which corresponds to the formation of the free pair of an electron and hole with the minimal kinetic energy. The origin of the maximum in emission is caused by the fact that with increasing energy also increases the density of energy states and simultaneously decreases the occurence of biexcitons [1]. The described approach to the exciton-exciton interaction based on the origination of biexciton corresponds to the situation in which the biexciton may be assumed as a stationary energetic state in the crystal. This occures at low temperatures.

At high temperatures when the life-time of exciton approaches to the scattering time is advantageous to assume the biexciton as a short lived state which is due to exciton-exciton collision. The life-time of this "compound" state must be longer than the scattering time of exciton on phonons. From this follows the binding energy of a such unstable biexciton will be transferred to the crystal lattice and the energy losses will depend on the duration of the exciton-exciton interaction with respect to the scattering time on phonons. In the limitting case it would be possible to suppose the mutual exciton-exciton interaction as a penetration of the exciton with another one. In this case the duration of interaction is given by radii and velocities of the interacting excitons. This hypothesis is analogues to the resonance reactions between elementary particles [21]. The life-time of such a compound state is in CdSe of about $2.6 \cdot 10^{-14}$ sec at $T = 300°$K and approximately $5 \cdot 10^{-14}$ sec at $T = 77°$K when we start from the equipartition theorem for the determination of exciton velocities. These life-times do not differ too much from the scattering times of excitons on the lattice vibrations. Experimental values for CdS are: $\tau_{300°K} = 2 \cdot 10^{-14}$ sec and $\tau_{77°K} = 9 \cdot 10^{-14}$ sec [22]. Energy losses during the scattering influence the position of the maximum of emission band. This maximum posesses stronger temperature dependence than the pure exciton emission [10], [11], [12], [13] (confr. Fig. 1). This is caused by the fact the ratio of life-time of biexciton to the scattering time of exciton increases with temperature. This approach to the phenomena of mutual interactions of excitons is the same as in [14] where is determined for low temperature region. Therefore the observed equivalence of our value $E^* = (1.812 \pm 0.002)$ eV

and the position of the emission maximum in [14] which amounts 1.811 eV for $T +$ $+ \langle 1.8 - 4 \rangle °K$ is not accidental.

It is well known there is a little probability of the spontaneous emission even at high concentration of interacting excitons. This creates the favorable conditions for the origin of stimulated emission in the biexcitonic emission band which has been already observed [12], [23].

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