

STRESS-INDUCED SPLITTING OF EMISSION LINES FROM  
EXCITONIC MOLECULES IN CdS AND ZnO

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ABSTRACT

Splittings of spontaneous emission lines in laser excited wurtzite-type CdS and ZnO are observed under a uniaxial stress at 1.8 K. The relative intensity of the split components of the excitonic molecule emission line is accounted for by using Hanamura's wave function for the excitonic molecule.

In the past few years, there have been extensive studies on various aspects of high density excitation effects in solids. The nature of an excitonic molecule has been one of the main points of interest to be clarified. Recently, it has been proved that an experiment on a uniaxial stress effect is very suited for the study of the excitonic molecule.<sup>1)</sup> Namely, we have observed the stress-induced splitting of the emission line which is ascribable only to the energy scheme of the excitonic molecule. This report deals with a detailed account of the experimental results and brief theoretical investigation of the uniaxial stress effect on the excitonic molecule in CdS and ZnO.

The experimental setup used has been already described.<sup>2)</sup> Figure 1 shows the emission and the reflection spectra on the (0001) plane of CdS under the uniaxial compression  $\sigma$  perpendicular to the C axis of the crystal. Since the wavevector  $k$  of the emitted light is parallel to the C axis, the spectra are completely unpolarized in the strain free crystals. Under the uniaxial stress  $\sigma \perp C$ , they split into two components with  $E \parallel \sigma$  and  $E \perp \sigma$ . The splitting patterns of the reflection spectrum and that of the M band are reversed as shown in Fig.1. In the reflection spectrum, the higher energy component is polarized with  $E \parallel \sigma$ . In the M band, on the contrary, the  $E \perp \sigma$  component is on the higher

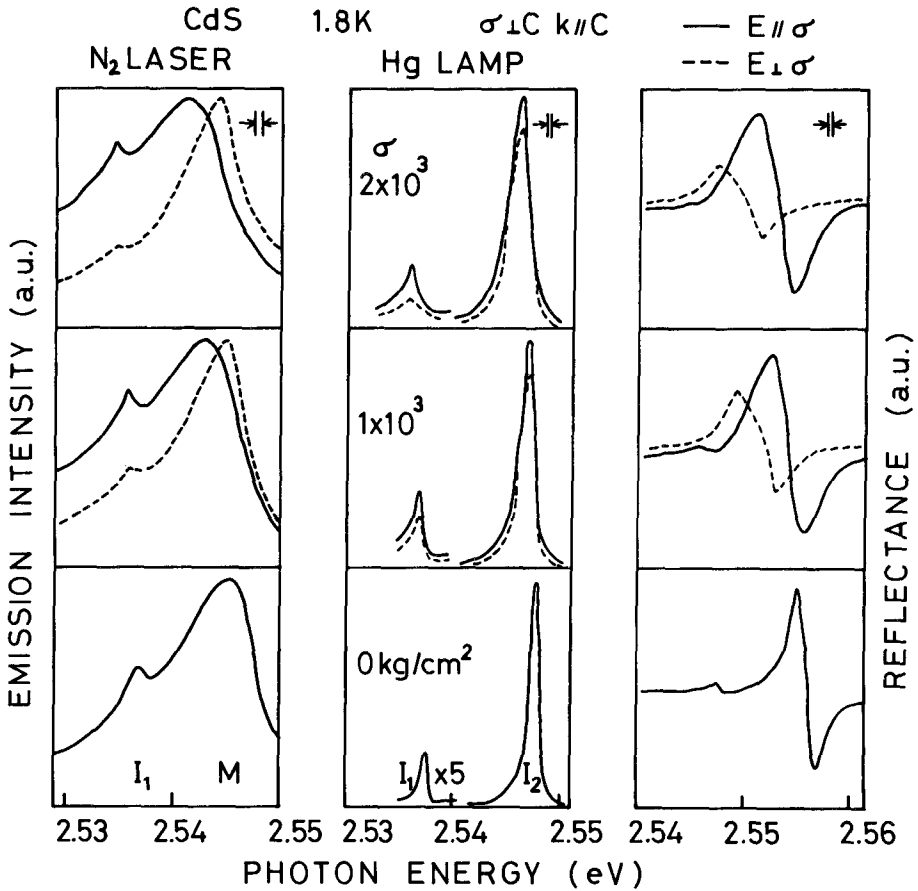


Fig.1. The change of the emission and the reflection spectra of CdS at 1.8 K. The intensity of the laser light on the surface of the sample is about  $0.2 \text{ MW/cm}^2$ . The intensities of the spectra are normalized with respect to the  $E/\sigma$  components.

energy side. This reversed splitting pattern of the M band is ascribable only to the energy scheme of the excitonic molecule.<sup>1)</sup> In this scheme, the initial state of the transition is the excitonic molecule ground state and the final state is the free exciton state. The splitting of the M band results from the splitting of the free exciton state. The intensity change of the split components is also different. The relative intensities of the split components are plotted against the applied pressure for the reflection spectrum, the M band and the bound

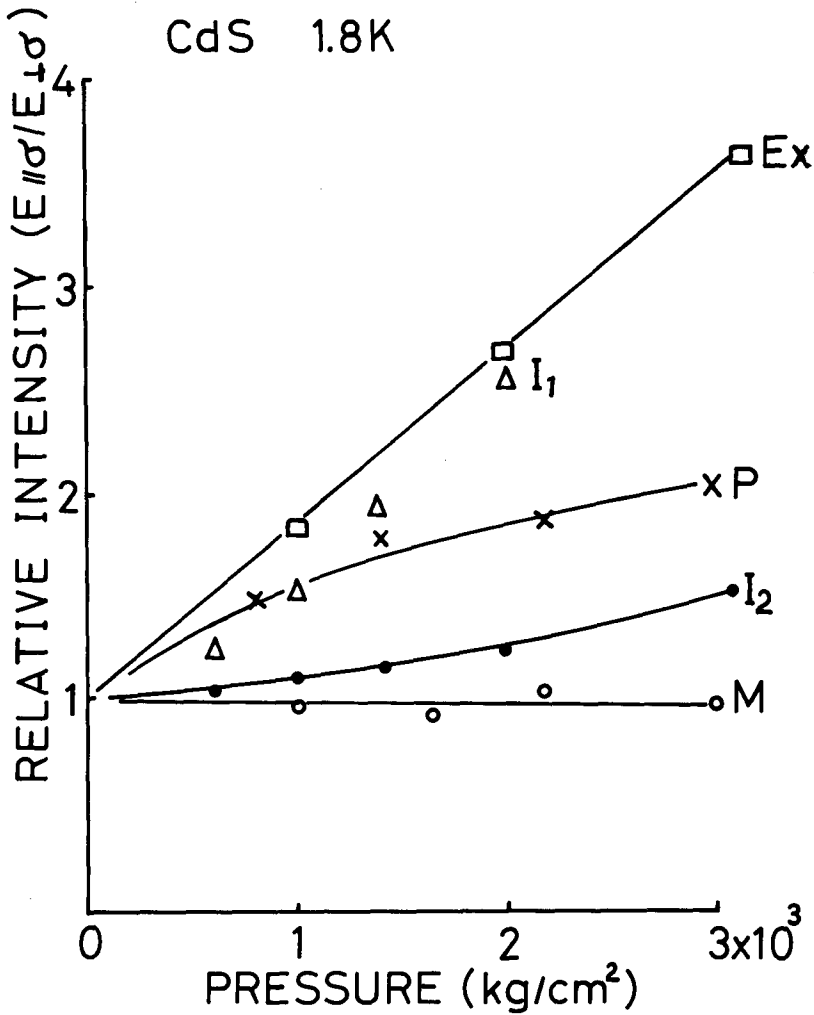


Fig.2. The relative intensity change of the  $E//\sigma$  and the  $E\perp\sigma$  components of the free exciton (Ex), the M band (M) and the bound excitons ( $I_1$  and  $I_2$ ). The stress effect of an emission from the free exciton scattering process is also shown (P).

exciton  $I_2$ ) in Fig.2. As shown in the figure, all emission bands except for the M band, as well as the reflection peak, show the decrease in the  $E\perp\sigma$  components with increasing pressure. In the M band, however, the relative intensity is nearly stress-independent. This is one of the

characteristic features of the M band in CdS. From Fig.1, the energies of the excitonic molecule ground state under the uniaxial stress can be determined by adding the energies of the split components of the exciton state and the M band. The resonant energies of the exciton state are taken from the reflection spectra. The obtained energy shift of the molecule ground state is shown in Fig.3. As is seen in the figure, the

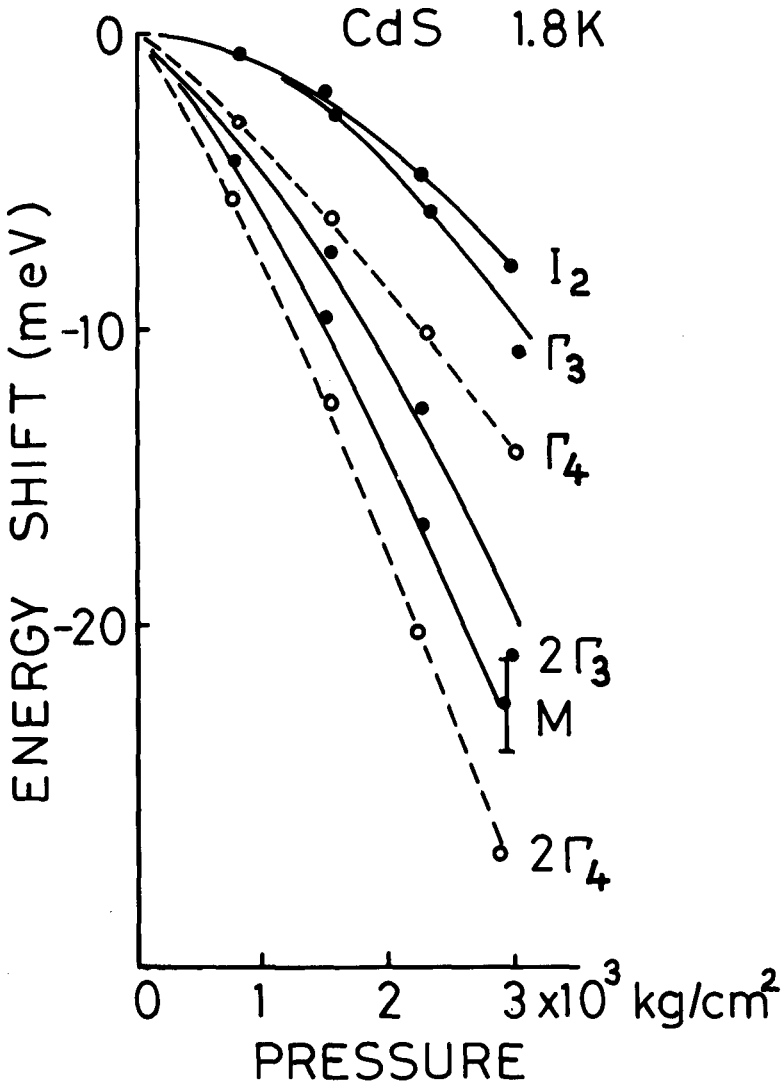


Fig.3. The energy shift of the  $\Gamma_3$  exciton ( $\Gamma_{5x}$ ,  $E//\sigma$ ),  $\Gamma_4$  exciton ( $\Gamma_{5y}$ ,  $E\perp\sigma$ ) and the excitonic molecule ground state (M) against the applied pressure.

molecule ground state does not show splitting within an experimental error. As shown in Fig.4, splitting has been observed also in the M

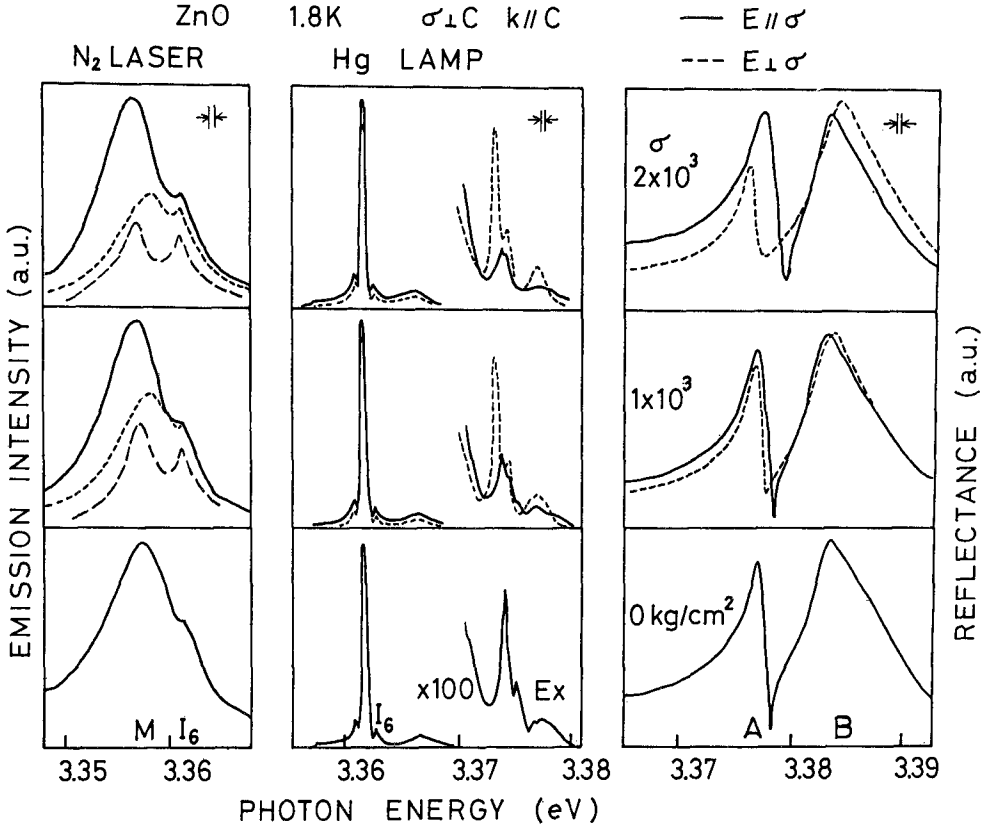


Fig.4. The changes of the emission and the reflection spectra of ZnO at 1.8 K. The exciting power of the laser is about  $1 \text{ MW/cm}^2$ . The intensities of the spectra are normalized to the  $E//\sigma$  components. In the spectra of the M band, long dashed curves show the  $E//\sigma$  component under lower excitation levels where the relative intensities of the M band and the  $I_6$  bound exciton are comparable with those of the  $E\perp\sigma$  component. In these cases, the splitting of the M band is still observable.

band of ZnO in the same geometry of  $\sigma\perp C$  and  $k//C$ . The behaviour of this band is qualitatively similar to that in CdS with regard to the polarization of the split components. However, the M band of ZnO show the same intensity change as that of the reflection anomaly of the A exciton. In both the lower energy reflection peak of the A exciton and the M band, the relative intensities of the  $E\perp\sigma$  components decrease with

increasing stress.

The splitting of the M band results from the splitting of the final state, and therefore, the relative intensity of the split components of the M band directly shows the transition probability between the excitonic molecule ground state and the free exciton state. In the stress-free crystals, CdS has  $C_{6v}$  symmetry at  $k=0$  and irreducible representations of the A exciton are  $\Gamma_5$  and  $\Gamma_6$ . The  $\Gamma_6$  exciton state is purely triplet and dipole forbidden. The  $\Gamma_5$  exciton is dipole allowed with E||C. In ZnO, the A exciton state is more complicated. According to the Hopfield's theory,<sup>3)</sup> the A exciton consists of three states,  $\Gamma_1$ ,  $\Gamma_2$  and  $\Gamma_5$ . The  $\Gamma_2$  exciton is dipole forbidden and the  $\Gamma_1$  exciton has a very weak oscillator strength with E//C. Under the uniaxial stress perpendicular to the C axis, the  $\Gamma_{5x}$  exciton and the  $\Gamma_{5y}$  exciton split by the combined effect of the spin-exchange and the uniaxial stress.<sup>4)</sup> In both CdS and ZnO, the  $\Gamma_{5x}$  state (E// $\sigma$  component) has a higher energy and a stronger oscillator strength as observed in the reflection spectra of CdS and ZnO. However, on the  $\Gamma_6$  state, the off-diagonal matrix elements of the spin-exchange Hamiltonian between the  $\Gamma_{6-}$  and  $\Gamma_{6+}$  states vanish. Therefore, we assume that the splitting of the  $\Gamma_6$  states is negligible because it arises from higher order interactions. The diagonal matrix elements of the stress Hamiltonian have the same form for the  $\Gamma_6$  and the  $\Gamma_5$  states, respectively, and the center of the gravities of the split  $\Gamma_5$  excitons and the  $\Gamma_6$  excitons shift parallel with each other under the uniaxial stress.

The excitonic molecule wave function has a symmetry of

$$\Gamma_{5x} \cdot \Gamma_{5x} - \Gamma_{5y} \cdot \Gamma_{5y} + \Gamma_{6-} \cdot \Gamma_{6-} - \Gamma_{6+} \cdot \Gamma_{6+} \quad (1)$$

as presented by Hanamura for CdS.<sup>5)</sup> In the same manner, for ZnO, the excitonic molecule wave function has a form of

$$\Gamma_{5x} \cdot \Gamma_{5x} - \Gamma_{5y} \cdot \Gamma_{5y} + \Gamma_1 \cdot \Gamma_1 - \Gamma_2 \cdot \Gamma_2 \quad (2).$$

From these wave functions, we can obtain two results. First, the ground

state energy of the excitonic molecule should not split under the uniaxial stress and stay between the double energies of the  $\Gamma_{5x}$  and the  $\Gamma_{5y}$  states. This proposal is consistent with our experimental result as shown in Fig.3. Second, the oscillator strength of the  $E//\sigma$  component ( $E\perp\sigma$ ) of the M band shows the same intensity dependence as that of the  $E//\sigma$  component ( $E\perp\sigma$ ) of the free exciton. This proposal is consistent with the result of ZnO as shown in Fig.4. But on CdS, this is not consistent. This fact seems to be attributable to the difference between the binding energies of the molecules in CdS and ZnO. The binding energy of the molecule in CdS is comparable with the splitting of the  $\Gamma_5$  exciton states at  $\sigma=3 \times 10^3 \text{ kg/cm}^2$ . Then the energy of the  $\Gamma_{5y}$  state (low energy component) approaches to the  $\frac{1}{2} \times$  (molecule ground state energy) under the uniaxial stress. On the other hand, the  $\Gamma_{5x}$  state shifts to the opposite energy side. Therefore, the weight of the  $\Gamma_{5y}$  exciton state in molecule wave function may become larger than that of the  $\Gamma_{5x}$  state and obscures the smaller oscillator strength of the  $\Gamma_{5y}$  component. In ZnO, the binding energy of the molecule is large compared with the splitting energy and this effect can be excluded.

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