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ABSORPTION OF THIN ZnSe, ZnS AND ZnS_xSe_{1-x} FILMS UNDER HIGH HYDROSTATIC PRESSURE*

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We present absorption measurements on free-standing ZnSe, ZnS and ZnS_xSe_{1-x} films ($d = 0.4 \dots 2 \mu\text{m}$) under hydrostatic pressure up to 15 GPa. The refraction index $n(\lambda, P)$ of ZnS and ZnSe in the transparent region up to 800 nm and the pressure shift of the E_0 absorption edge of ZnSe and some ZnS_xSe_{1-x}-compositions was investigated at 293 K. At 2 K free exciton states near the E_0 - and $E_0 + \Delta_0$ -gap are visible in absorption. Increase in the Rydberg energy under pressure was found, which is explained with $k \cdot p$ -theory in the framework of the hydrogen model.

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1. Samples and experimental setup

Cubic samples were grown by metalorganic vapour phase epitaxy (MOVPE) or MBE on (001)-orientated GaAs. The substrate was removed in two steps. First, the GaAs was mechanically polished to a thickness of about 50 μm , then the remaining GaAs was etched off selectively by a 82% n -NaOH and 18% H₂O₂ (30%) mixture. The investigations under hydrostatic pressure have been performed in a gasketed diamond anvil cell (DAC) with liquid He as pressure transmitting medium. Ruby fluorescence was used for pressure calibration.

2. Results and discussion

2.1. Pressure dependence of the refractive index of ZnSe, ZnS

The refractive index $n(\lambda, P)$ was measured by analyzing the interference pattern of MOVPE-samples with plane-parallel surfaces (thickness $\approx 2 \mu\text{m}$). The maxima and minima in the transparent region ($\alpha = 0$) are given by

$$2n(\lambda, P)d = m\lambda, \quad m = \frac{1}{2}, 1, \frac{3}{2}, 2, \dots \quad (1)$$

where d is the sample thickness, m — the order of the interference and λ — the wavelengths of the interference extrema. At $P = 0$ we used well known curves of

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$n(\lambda)$ (ZnSe: [1], ZnS: [2]) to determine d and m . The interference pattern shifts under pressure. We kept track of the extrema and calculated $n(\lambda, P)$ at these wavelengths using Eq. (1). The decrease in thickness d , given by the Murnaghan equation [3]

$$d(P)/d_0 = (1 + B'_0 P/B_0)^{-1/(3B'_0)}, \quad \lambda : [\mu\text{m}] \quad (2)$$

was taken into account. Values used for the isothermal bulk modulus and its pressure derivative are $B_0 = 62.4$ GPa, $B'_0 = 4.77$ for ZnSe [4] and $B_0 = 75.0$ GPa, $B'_0 = 4.0$ for ZnS [5]. Marple's formula [1], describing the refractive index dispersion, was fitted to the experimental data

$$n^2(\lambda) = \epsilon(\lambda) = A(P) + \frac{B(P)\lambda^2}{\lambda^2 - C(P)}, \quad (3)$$

where $A(P)$, $B(P)$ and $C(P)$ are semiempirical parameters, given by ZnSe:

$$A(P) = (4.05 \pm 0.1) - (0.015 \pm 0.01)P \frac{1}{\text{GPa}},$$

$$B(P) = (1.84 \pm 0.1) + (0.01 \pm 0.01)P \frac{1}{\text{GPa}},$$

$$C(P) = (0.114 \pm 0.005)\mu\text{m}^2 - (4.5 \pm 0.5)10^{-3}P \frac{\mu\text{m}^2}{\text{GPa}} \\ + (1.2 \pm 0.2)10^{-4}P^2 \frac{\mu\text{m}^2}{\text{GPa}^2},$$

ZnS:

$$A(P) = (3.7 \pm 0.1) - (0.065 \pm 0.01)P \frac{1}{\text{GPa}},$$

$$B(P) = (1.45 \pm 0.1) + (0.06 \pm 0.01)P \frac{1}{\text{GPa}},$$

$$C(P) = (0.072 \pm 0.003)\mu\text{m}^2 - (1.9 \pm 0.4)10^{-3}P \frac{\mu\text{m}^2}{\text{GPa}}.$$

As $\lambda \rightarrow \infty$, (3) yields the high frequency dielectric constant $\epsilon_\infty = A(P) + B(P)$. We obtained $\epsilon_\infty(\text{ZnSe}) = 5.9 \pm 0.2$ and $\epsilon_\infty(\text{ZnS}) = 5.15 \pm 0.2$ for all applied pressures. Obviously ϵ_∞ of ZnSe and ZnS is independent of pressure.

2.2. Absorption of $\text{ZnS}_x\text{Se}_{1-x}$ at 293 K

The effects of hydrostatic and biaxial strain on the heavy hole (hh)-, light hole (lh)- and split off (so)- band are given by the following equations [6]:

$$E_{\text{hh}'}(\epsilon_{\text{hyd}}, \epsilon_{\text{bi}}) = E_0 + \delta E_{\text{h}} + \delta E_{\text{s}},$$

$$E_{\text{lh}'}(\epsilon_{\text{hyd}}, \epsilon_{\text{bi}}) = E_0 + \delta E_{\text{h}} + \frac{1}{2}(\Delta_0 - \delta E_{\text{s}}) - \frac{1}{2}\sqrt{\Delta_0^2 + 2\Delta_0\delta E_{\text{s}} + 9\delta E_{\text{s}}^2},$$

$$E_{\text{so}'}(\epsilon_{\text{hyd}}, \epsilon_{\text{bi}}) = E_0 + \delta E_{\text{h}} + \frac{1}{2}(\Delta_0 - \delta E_{\text{s}}) + \frac{1}{2}\sqrt{\Delta_0^2 + 2\Delta_0\delta E_{\text{s}} + 9\delta E_{\text{s}}^2}, \quad (4)$$

where

$$\delta E_{\text{h}} = a \left(3\epsilon_{\text{hyd}} + \left(2 - \frac{2C_{12}}{C_{11}} \right) \epsilon_{\text{bi}} \right); \quad \delta E_{\text{s}} = -b \left(1 + \frac{2C_{12}}{C_{11}} \right) \epsilon_{\text{bi}},$$

and a , b are the deformation potentials, ϵ_{hyd} , ϵ_{bi} — the hydrostatic and biaxial strain, C_{11} , C_{12} — the elastic constants.

At 293 K the applied pressure is purely hydrostatic. In this case we derive from (4):

$$E_{\text{hh, lh}}(\epsilon_{\text{hyd}}) = E_0 + 3a\epsilon_{\text{hyd}} \quad \text{and} \quad E_{\text{so}}(\epsilon_{\text{hyd}}) = E_0 + \Delta_0 + 3a\epsilon_{\text{hyd}}.$$

The pressure shift of the fundamental absorption edge $E_0(P)$ and of $(E_0 + \Delta_0)(P)$ (Fig. 2a for ZnSe) is well described by a quadratic function $E_0(P) = E_0 + \alpha P + \beta P^2$ (see Table for ZnSe and ZnS_xSe_{1-x}). Using the Murnaghan equation (2) and the definition of hydrostatic strain $\epsilon_{\text{hyd}} = \frac{d(P)}{d_0} - 1$, we obtain $E_0(\epsilon)$ from $E_0(P)$.

A linear fit of the experimental data yields $a = -4.9 \pm 0.1$ eV for ZnSe.

2.3. ZnSe: absorption at 2 K

Using rather thin samples ($d = 0.4 \mu\text{m}$), pressure shift of 1s-free excitons near the E_0 and $E_0 + \Delta_0$ -gap were investigated (Fig. 1). An unintentional splitting of the hh- and lh-components occurred under pressure, caused by a small biaxial strain ϵ_{bi} in the (001)-plane due to the freezing of the helium in the DAC.

Using Eqs. (4), $C_{11} = 85.9$ GPa, $C_{12} = 50.6$ GPa from [7], $\Delta_0 = 0.432$ eV and a from this work, $b = -1.14$ eV $- 0.17P \frac{\text{eV}}{\text{GPa}}$ from [8], it is possible to separate the hydrostatic and biaxial strain. Results, obtained from a best fit of E_0 and $E_0 + \Delta_0$ -excitons are given in Table. Assuming that the Rydberg energy of excitons at the E_0 - and $E_0 + \Delta_0$ -gap changes in the same way, we obtain $\Delta_0(P)$.

2.4. Pressure dependence of the Rydberg energy

The theoretical model: The increase in the Rydberg energy $R(P)$ is understood in the framework of the hydrogen model

$$R(P) = R_{\text{hydrogen}} \frac{\mu_0(P)}{m_0 \epsilon_{\text{st}}(P)^2} \quad \text{where} \quad \mu_0(P) = \left(\frac{1}{m_c(P)} + \frac{\gamma_1(P)}{m} \right)^{-1}. \quad (5)$$

The change of the static dielectric constant ϵ_{st} is calculated with the Lyddane-Sachs-Teller relation $\epsilon_{\text{st}} = \epsilon_\infty \frac{\omega_{\text{LO}}^2(P)}{\omega_{\text{TO}}^2(P)}$ taking $\omega_{\text{LO}}^2(P)$, $\omega_{\text{TO}}^2(P)$ from [11] and ϵ_∞ from this work. The pressure dependence of m_c and γ_1 is taken into account below (8), (9).

Cubic correction: At pressures up to 8 GPa, the 2s-hh-absorption peak was visible. In order to compare the measured $E_{1s} - E_{2s}$ with R from (5), deviations of hyperbolic bands had been taken into account. The binding energies for the 1s- and 2s-excitons were calculated by Balderechi and Lipari [9]:

$$\begin{aligned} E_{1s} &= R \left[1 + \frac{4}{5} \left(8 \frac{\mu_0^2 \gamma_2^2}{m^2} + \frac{12 \mu_0^2 \gamma_3^2}{m^2} \right) S_1(\Delta_0) \right], \\ E_{2s} &= R \left[\frac{1}{4} + \frac{1}{5} \left(4 \frac{\mu_0^2 \gamma_2^2}{m^2} + \frac{6 \mu_0^2 \gamma_3^2}{m^2} \right) S_2(\Delta_0) \right]. \end{aligned} \quad (6)$$

At zero-pressure $\gamma_1 = 2.45$, $\gamma_2 = 0.61$, $\gamma_3 = 1.11$ and $m_c = 0.147$ are taken from [10], pressure dependence: see (8), (9). The functions $S_1(\Delta_0)$ and $S_2(\Delta_0)$ are supposed to be pressure-independent (ZnSe: $S_1 = 0.2587$, $S_2 = 0.7543$).

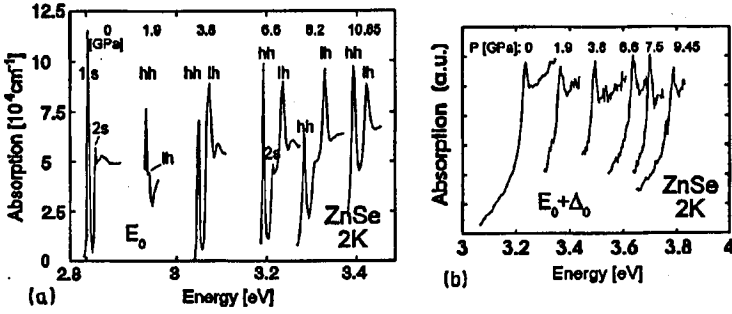


Fig. 1. (a) Shift of excitonic absorption near the E_0 -gap under hydrostatic pressure at 2 K. The split up of lh- and hh-excitons at E_0 is due to biaxial strain, caused by the freeze of the pressure medium. The 2s-hh-exciton at E_0 is visible up to 6.6 GPa. (b) Pressure shift of the excitonic absorption near the $E_0 + \Delta_0$ -gap at 2 K.

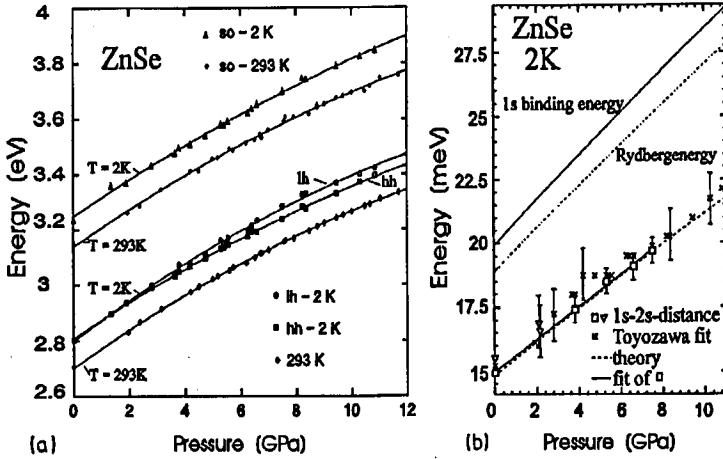


Fig. 2. (a) Pressure shift of excitonic absorption near the E_0 and $E_0 + \Delta_0$ -gap. (b) Change of Rydberg energy at 2 K. $E_{1s} - E_{2s}$ is derived directly from the distance of 1s- and 2s-excitons (two samples: squares, triangles) and from a fit first mentioned by Toyozawa [14] (\times). The lower dashed line shows the 1s-2s distance, derived from the theoretical model.

Pressure dependence of m_c , γ_1 , γ_2 and γ_3 : In order to obtain $m_c(P)$, we calculate the strain dependence of the effective mass tensor given by J.M. Luttinger [12]:

$$\frac{1}{m_c(\epsilon)} = \frac{1}{m} + \frac{2}{m^2} \sum_{n' \neq n} \frac{|\hat{i} \cdot p_{n,n'}(\epsilon)|^2}{E_n(\mathbf{k} = 0, \epsilon) - E_{n'}(\mathbf{k} = 0, \epsilon)}. \tag{7}$$

After transforming $|p_{n,n'}(\epsilon)| = \frac{1}{1+\epsilon} |p_{n,n'}(\epsilon = 0)|$ [13] and eliminating $|p_{n,n'}(\epsilon = 0)|$

TABLE

Pressure coefficients of E₀- and E₀ + Δ₀-excitons, Δ₀ and R.

Sample		T [K]	E [meV]	dE/dP [$\frac{\text{meV}}{\text{GPa}}$]	d ² E/dP ² [$\frac{\text{meV}}{\text{GPa}^2}$]
ZnSe	E ₀	293	2700 ± 5	70 ± 2	-1.4 ± 0.1
	E ₀ + Δ ₀	293	3138 ± 5	70 ± 4	-1.4 ± 0.1
	E ₀	2	2807 ± 3	67 ± 4	-1.4 ± 0.1
	Δ ₀	2	432 ± 5	0.4 ± 0.2	-
	R	2	20 ± 0.5	0.8 ± 0.1	-
ZnS _{0.13} Se _{0.87}	E ₀	293	2781 ± 4	69 ± 2	-1.4 ± 0.1
ZnS _{0.31} Se _{0.69}	E ₀	293	2904 ± 5	65 ± 2	-1.2 ± 0.1
ZnS _{0.46} Se _{0.54}	E ₀	293	3075 ± 6	62 ± 2	-1.2 ± 0.2

by inserting $m_c(\epsilon = 0)$, we obtain

$$\frac{1}{m_c(\epsilon)} = \frac{1}{m} + \left(\frac{m - m_c(\epsilon = 0)}{mm_c(\epsilon = 0)} \right) \epsilon_c(\epsilon) \text{ with } \epsilon_c(\epsilon) := \frac{E_0(\epsilon = 0)}{E_0(\epsilon)} \frac{1}{(1 + \epsilon)^2}. \quad (8)$$

In the same way we estimate the change of the Luttinger parameters [12]:

$$\gamma_1(\epsilon) = 1 + [\gamma_1(\epsilon = 0) - 1]\epsilon_c(\epsilon), \quad \gamma_2(\epsilon) = \gamma_2(\epsilon = 0)\epsilon_c(\epsilon),$$

$$\gamma_3(\epsilon) = \gamma_3(\epsilon = 0)\epsilon_c(\epsilon). \quad (9)$$

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