# Size quantization of excitons in CdTe

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An increase in the binding energy of a free exciton is observed in CdTe thin films. This increase results from a decrease in the screening of the Coulomb interaction in electron-hole pairs. The observed change in the exciton binding energy agrees satisfactorily with theoretical predictions.

The transition from bulk crystals to thin films is accompanied by a radical change in the energy spectrum of both free charge carriers and bound states. The energy spectrum of free carriers changes when the film thickness $d$ becomes comparable to the de Broglie wavelength of electrons in the crystal. Motion in the direction across the film can be assumed bounded, and the energy spectrum in this direction becomes discrete:

$$\Delta E_n = \frac{\pi^2\hbar^2}{2m^*d^2}\, n^2, \quad n = 1, 2, 3 \ldots \tag{1}$$

where $m^*$ is the effective mass of the electron (or hole). As was shown in Ref. 1, however, a quantitative description of size quantization of free carriers in thin semiconducting films definitely requires consideration of the thickness dependence of the effective mass and also of the finite depth of the potential well.

An important change in the energy spectrum of bound states (of Wannier-Mott excitons, for example) occurs if $d \leqslant a_0$ ($a_0$ is the first Bohr radius of the $3D$ exciton), and the dielectric constant ($\epsilon$) of the film is either much greater than or much less than $\epsilon_1$ and $\epsilon_2$—the dielectric constants of the media surrounding the film.[2] As the film thickness is reduced to $d \leqslant a_0$, the field produced by the electron and the hole which are bound in an exciton begins to penetrate into the medium surrounding the film. If $\epsilon_{1,2} \ll \epsilon$, the screening of the Coulomb interaction between the charges is reduced, with the result that the exciton binding energy $\mathscr{E}_{\text{exc}}(d)$ increases, while the effective exciton radius $a$ decreases. It was shown in Ref. 3 that under the conditions $a_0\delta^2 \ll d \ll a_0$ the exciton energy levels are given by

$$\mathscr{E}_{n,m}(d) = -\frac{e^2}{\epsilon d}\left(\ln\frac{4d}{\delta^2 a_0} - 2\gamma_{n,m} - 2C\right), \tag{2}$$

where $n$ and $m$ are the main and orbital quantum numbers, $\delta = (\epsilon_1 + \epsilon_2)/2\epsilon$, $C = 0.577$ is Euler's constant, and $\gamma \approx 1$. Furthermore, under the conditions $d \leqslant a_0$ and $\epsilon_{1,2} \ll \epsilon$ the decrease in the binding energy and the decrease in the effective radius should cause the oscillator strength to increase sharply with decreasing thickness.[4] This circumstance apparently makes it much simpler to measure the characteristics of

  

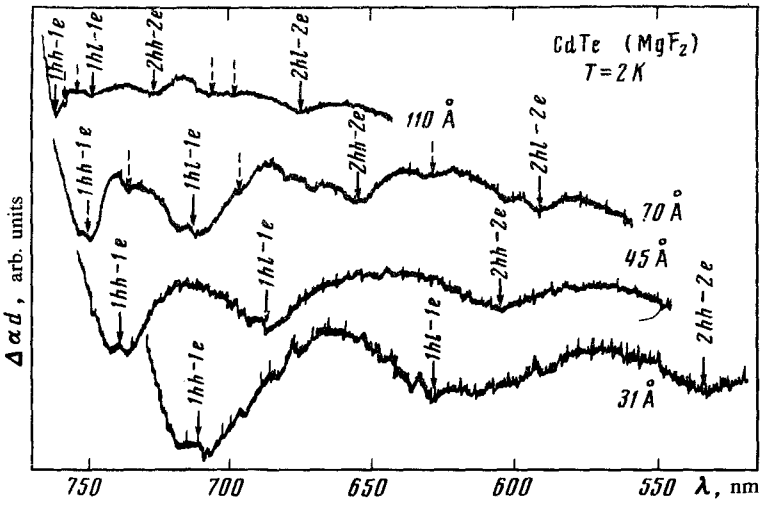


FIG. 1. Spectrum of the change in the optical density of CdTe films of various thicknesses.

light transmission by thin films, for which the condition $\alpha d \ll 1$ holds ($\alpha$ is the absorption coefficient of the crystal).

Several attempts have been made to study the change in the exciton binding energy in thin single layers of semiconductors.[5–7] Layered $WSe_2$ and GaSe crystals were studied by Consadori and Frind[5] and Abdullaev *et al.*[6] They apparently observed a significant increase in the free-exciton binding energy. However, it is not possible to quantitatively compare their experimental results with the theory, since the thickness was determined from measurements of the optical density in the strong absorption region without allowance for the substantial change in the free-carrier energy spectrum due to size quantization.

In the present letter we report a study of the size quantization of CdTe single-crystal films on an $MgF_2$ substrate over the thickness range from 250 to 30 Å at $T = 2$ K. The measurements were based on the optical absorption spectra. The films were synthesized by laser deposition with a subsequent recrystallization annealing. Using the special method which we proposed in Ref. 1, we observed exciton states (minima) associated with quantized electron and hole bands in the spectra of $\Delta\alpha d$ (Fig. 1). The optical transitions were identified by the method of Ref. 1. We see that as $d$ is reduced, the minima in the spectra shift toward shorter wavelengths, while the energy interval between the minima increases, in qualitative accordance with (1). We also see a splitting of the first minimum, and this splitting increases with decreasing $d$. At present, however, we cannot offer a quantitative explanation for this effect. The splitting observed experimentally is probably due to a change in the volume interaction of the electron and the hole in the exciton at small thicknesses.

Of decisive importance to the quantitative interpretation of the experimental data is the circumstance that we were able to observe exciton states belonging to high-index bands ($n = 2$, 3). It thus becomes possible to determine $d$ independently from the ellipsometric measurements.[1] Theoretical curves of the size quantization of the band

states were generated by numerical calculations. The equations on which these calculations were based incorporated a renormalization of the effective masses of the electrons and light holes and the finite depth of the potential well, equal to the work function. These equations are

$$E_g = E_{g0} + \frac{2\hbar^2 n^2}{m^*(d)d^2} f(x)$$

$$\frac{m}{m_e^*} = 1 + \frac{P^2}{2D}\left[\frac{D + D_H}{3}\left(\frac{2}{E_g} + \frac{1}{E_g + \Delta_{so}}\right) - \frac{D - D_H}{D - E_g}\right],$$

$$\frac{m}{m_{hl}^*} = \frac{2P^2}{3E_g} - 1,$$

where $x$ is given as a function of $\zeta = \varphi/(2\hbar^2/m^*(d)'d^2$ by

$$\begin{cases} x = \arctan\sqrt{\zeta/x^2 - 1} & (n = 1) \\ x = \pi - \arctan\dfrac{1}{\sqrt{\zeta/x^2 - 1}} & (n = 2) \end{cases}$$

In the numerical calculations we used the values $P^2 = 21$ eV, $\Delta_{so} = 0.92$ eV, $D = E(\Gamma_{15c}) - E(\Gamma_{15v})$ eV, $D_H = E(\Gamma_{15}) - E(\Gamma_{25'}) = 3.2$ eV, and the work function $\varphi$ for CdTe (4.5 eV).

Figure 2 shows the experimental energy shifts of the excitons belonging to the various bands, along with calculated curves of the size quantization of the band states.

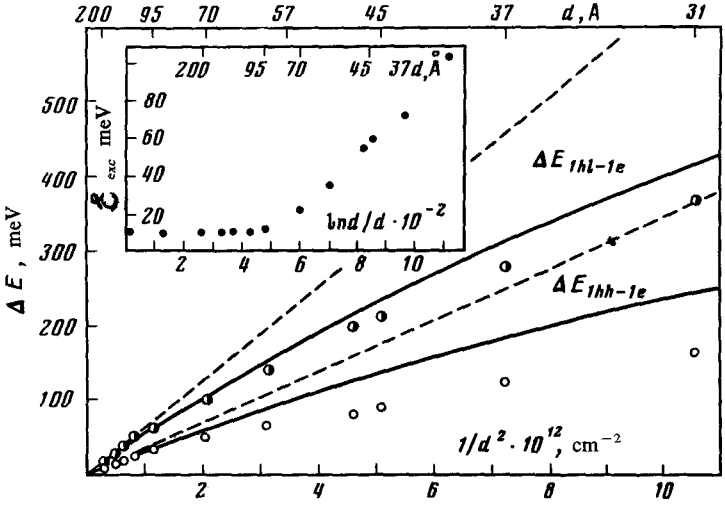


FIG. 2. Energy positions of the size-quantization levels versus the thickness of the CdTe film. Solid lines—Calculated curves of the size quantization of band states with renormalization of the effective masses and a finite potential well depth; dashed lines—calculations from expression (1) without corrections. The points are experimental.

We see that at thicknesses greater than $\sim 80$ Å the experimental points conform well to the theoretical curves. For large thicknesses the shift of the exciton ground state thus corresponds precisely to the change in the width of the energy gap due to size quantization, while the binding energy of the exciton does not change. As the thickness $d \leqslant a_0$ is reduced, the experimental points deviate progressively from the theoretical curves; this behavior corresponds to a substantial increase in the binding energy of the free exciton. The inset in Fig. 2 shows the exciton binding energy $\mathscr{E}_{\text{exc}}(d)$ found from these data (for the $1hh$–$1e$ subbands) versus $d$. It should be noted that the change in the exciton binding energy is a nearly linear function of $\ln d/d$, in qualitative agreement with the theory [see expression (2)].

The experimental and theoretical[3] results agree reasonably well in the range of applicability of the theory ($d \simeq 40$ Å): $\mathscr{E}_{\text{exc}}^{\text{teo}}(40\text{ Å}) \simeq 40$ meV and $\mathscr{E}_{\text{exc}}^{\text{expt}}(40\text{ Å}) \simeq 60$ meV.

The value of $\mathscr{E}_{\text{exc}}^{\text{teo}}$ was found for $1/\delta = 3$ and $2\gamma_{\text{nm}} + 2C = 2.2$.

In summary, these experiments confirm that the energy spectrum of bound states in a semiconducting thin film depends strongly on the dielectric constants of the media bounding the film.

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