Dispersion of refractive index in thin films CdI_2 and ZnI_2

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The refractive index dispersion in thin CdI_2 and ZnI_2 films has been measured in the wavelength interval 300–1000 nm and processed using the monooscillator model agreeing well with experimental data. The optical permittivity ε_∞ of both compounds has been determined using the found parameters of this model, the optical permittivity data have been used in the further analysis of exciton states in CdI_2 and ZnI_2, in particular, for determination of $1s$ exciton radius. The found a_{ex} values are close to the unit cell parameters of the compounds, thus indicating that the excitons in two compounds belong to excitons of the intermediate electron-hole bond.

В тонких пленках CdI_2 и ZnI_2 измерена дисперсия показателя преломления в интервале длин волн 300–1000 нм, и полученные результаты обработаны с применением одноосцилляторной модели, хорошо согласующейся с данными эксперимента. По найденным параметрам этой модели определена оптическая диэлектрическая проницаемость ε_∞ обоих соединений, использованная для дальнейшего анализа экситонных состояний в CdI_2 и ZnI_2 и, в частности, для определения радиуса $1s$-экситонов. Найденные значения a_{ex} близки к параметрам элементарной ячейки соединений, что указывает на принадлежность экситонов в обоих соединениях к экситонам промежуточной электрон-дырочной связи.

1. Introduction

The compounds CdI_2 and ZnI_2 are layered dielectrics consisting of close-packed I–Me–I packets with ionic bonding predominating therein, coupled to other packets by a weak Van-der-Waals interaction. The crystal structure of CdI_2 was studied by numerous authors. This compound tends to formation of polytypes. The most common polytypes are 2H and 4H. Both polytypes have a hexagonal unit cell with $a = 4.24$ Å, $c = 6.24$ Å for the 2H polytype and $c = 13.68$ Å for the 4H-polytype (with 2 molecules per unit cell). All the polytypes are transformed in 4H under crystal annealing [1, 2]. The structure of ZnI_2 is less studied. According to some data [3], ZnI_2 has the structure of the 2H CdI_2 polytype with lattice constants $a = 4.25$ Å

and $c = 6.54$ Å; other data show that ZnI_2 forms the $CdCl_2$ type crystal lattice with three molecules per unit cell [4]. The second structural type ($CdCl_2$) is based on the close cubic packaging of layers, each 4-th layer being repeated in an identical position, but packets-sandwiches in this type are identical to those in CdI_2 [2]. The fundamental electron spectrum of CdI_2 has been investigated explicitly enough in [5–8]. It has been established that CdI_2 is an indirect-gap dielectric [6, 8], with the gap width $E_g = 3.473$ eV, while the energy gap corresponding to direct transitions between the valence band and conductance one is close to 4 eV. In [9], the optical constants have been calculated for CdI_2 single crystals in the 4–10 eV range. In the transparence region, the refractive index for two polarisations

has been determined from the transmittance spectra of a thin CdI_2 crystal plate [10]. As far as we know, there are no data on optical constants of the thin polycrystal CdI_2 films in the transparence range. The compound ZnI_2 is highly hygroscopic. This compound seems to be little studied just for that reason. The absorption spectrum of thin ZnI_2 films has been studied in [11]. It is established that, in contrast to CdI_2, ZnI_2 is an direct-gap dielectric with the gap width $E_g = 4.62$ eV [11]. However, optical constants (refractive index n and absorption index κ) of thin ZnI_2 films were not calculated, and we have not met such data in the literature.

It is of interest to compare the dispersion dependences of refractive index for the thin CdI_2 polycrystal films and crystals as well as the refractive index dispersion in structurally similar thin ZnI_2 films. In this study, the measured data on refractive index n in thin CdI_2 and ZnI_2 polycrystal films in the transparence range up to 1000 nm are presented as well as the experimental data processing based on the monooscillator model. The experimental results have been used to analyse the exciton spectra of both compounds.

2. Experimental

The CdI_2 and ZnI_2 thin films were prepared by vacuum deposition of CdI_2 and ZnI_2 powders onto quartz substrates heated up to 80°C. Then the samples were annealed for 1 h at the same temperature. This preparation method seems to provide the formation of CdI_2 4H polytype [1]. No structure studies were carried out. However, the above sample preparation method is similar to that described in [12], where structure studies of thin CdI_2 films were realized. According to [12], the CdI_2 films prepared in that manner show a high structural perfection. The crystallites of several micrometers in size are oriented with their **c** axes perpendicular to the substrate. Apparently, the same can be stated for ZnI_2 films, since the preparation conditions thereof are the same as for CdI_2 and crystal structures of the compounds are similar. Due to high hygroscopicity of ZnI_2, a strong light scattering arises in the films removed from vacuum chamber and cooled to room temperature. To avoid this, the samples in the heated state were transferred to a vacuum optical cryostat with copper finger heated previously to 70°C. After the cryostat was

pumped down, the films remained transparent and suitable for spectral measurements.

The transmission spectra of the films were measured in the 1.2–4.1 eV spectral range at room temperature (290 K) using an SF-46 spectrophotometer with reference to a quartz plate of the thickness equal to the substrate one. The film thickness t was determined from transmission spectra in their transparence region with taking into account the light interference by the method from [13]. The film thickness selection (300–400 nm for ZnI_2 and 400–550 nm for CdI_2) was dictated by the method used to determine the refractive index dispersion [13] as a maximum layer thickness at which there is yet no light scattering in films. The thickness of CdI_2 films was monitored in addition by a Linnik interferometer.

3. Results and discussion

The transmission of a thin film T in the transparence range where condition $n \gg \kappa$ is met, κ is the absorption index, is determined by a expression

$$T = \frac{16n^2 n_1 \eta n_0}{c_1^2 + c_2^2 \eta^2 + 2c_1 c_2 \eta \cos\dfrac{4\pi n t}{\lambda}} \qquad (1)$$

where $c_1 = (n+n_0)(n_1+n)$, $c_2 = (n-n_0)(n_1-n)$, $\eta = \exp(-Kt)$; n_1 is the substrate refractive index; n_0, that of the air; K, the extinction coefficient. In absence of a light scattering, $K = 4\pi k/\lambda$.

In the transparence region, the dispersion of constants is as a rule insignificant, therefore, the transmission extremes are reached at

$$4\pi n t/\lambda = m\pi, \qquad (2)$$

where m means even integers for maxima and odd for minima. For a particular case $n > n_1$, which is realized for CdI_2 and ZnI_2, the transmission extremes are determined by formulas

$$T_{\max} = \frac{16 n_0 n_1 n^2 \eta}{(c_1 + c_2 \eta)^2}, \qquad (3a)$$

$$T_{\min} = \frac{16 n_0 n_1 n^2 \eta}{(c_1 - c_2 \eta)^2}. \qquad (3b)$$

When taking into account the dependences of optical constants on the wavelength, the condition (2) gives the points of contact of maxima (m is even) and minima
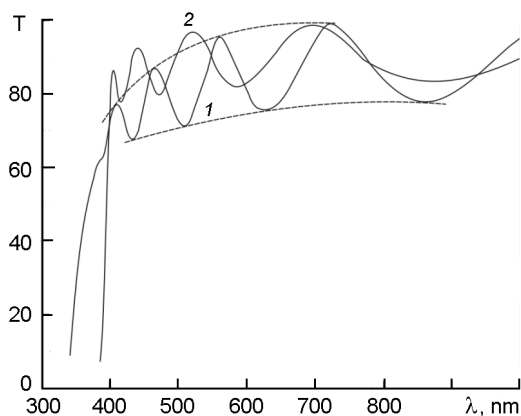
Fig. 1. A typical transmittance spectrum of CdI_2 (1) ($t = 520$ nm) and ZnI_2 (2) ($t = 339$ nm) thin films on a quartz substrate.

Fig. 2. Spectral dependences of the refractive index $n(\lambda)$ for CdI_2 (1) and ZnI_2 (2) thin films. Points are the experimental data, solid curves are calculated using formula (4).

Fig. 3. The dependences $(n^2-1)^{-1}$ on E^2 for CdI_2 (1) and ZnI_2 (2) thin films.

(m is odd) envelopes in the $T(\lambda)$ dependence (Fig. 1), while the formulas (3a, b) can be considered as equations of maxima and minima envelopes. The film thickness is found from the condition (2), having previously defined the order of interference m from a spectral position of two adjacent maxima or minima. The value $n(\lambda)$ is determined using formula (2) for the points conforming to spectral position T_{max} and T_{min} and known order m.

The dispersion of refractive index $n(\lambda)$ of thin films is determined from the transmission spectra of CdI_2 and ZnI_2 films using the above method [13] (Fig. 2). Since the ZnI_2 films is relatively thin and there are few extrema within the measured λ range, several samples of different thickness were examined to increase the accuracy of $n(\lambda)$ determination. CdI_2 and ZnI_2 are optically anisotropic crystals and birefringence should be observed therein. But, as it was already noted above, in our films, the crystallites are oriented with their **c** axes perpendicular to the substrate. At the normal light incidence on the sample, i.e. along an **c** axis, there is no birefringence.

The dispersion of the real dielectric permittivity part in the CdI_2 and ZnI_2 films in the transparence range is well described by a monooscillatory model [14]:

$$\varepsilon_1 = n^2 = 1 + \frac{E_d E_0}{E_0^2 - E^2}, \qquad (4)$$

where $E = \hbar\omega$, E_0 and E_d are the monooscillatory model parameters. E_0 determines the spectral position of the effective oscillator associated with interband optical transitions; the value $E_0 > E_g$ and its position is
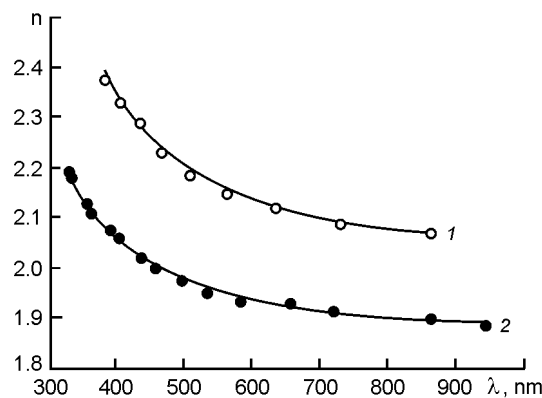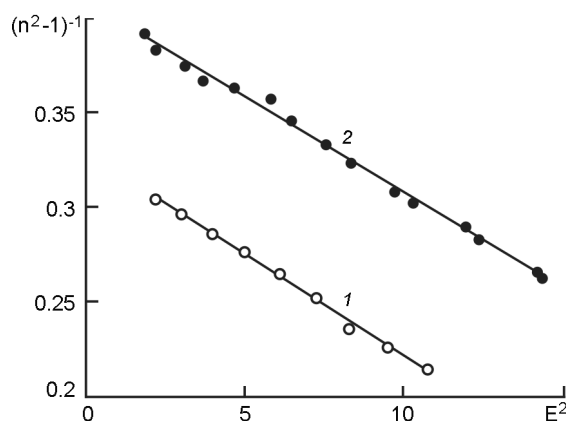
close to the maximum of the electron absorption band. E_d is the dispersion energy describing the force of interband transitions. The formula (4) was used to interpret the experimental $n(\lambda)$ data for different materials, both crystalline and amorphous [14, 15] and conforms well with experiment.

The dependence (4) is linear in $(n^2-1)^{-1}-E^2$ coordinates. The interpretation of $(n^2-1)^{-1}-E^2$ (Fig. 3) by the least squares method has allowed to determine the value $(E_0 E_d)^{-1} = 0.011\pm0.0002$; 0.01 ± 0.0002 (using the straight slope) and value $E_0/E_d = 0.328\pm0.0015$; 0.407 ± 0.0015 (using the crossing with the ordinate axis) for CdI_2 and ZnI_2 films, respectively. Therefrom, $E_0 = 5.46$; 6.38 eV and $E_d = 16.65$; 15.67 eV for CdI_2 and ZnI_2 films, respectively. The $n(\lambda)$ dependence calculated using the formula (4) the above E_0 and E_d is in fair agreement

Table. The parameters of monooscillator model and excitons in CdI_2 and ZnI_2

Compound	E_0, eV	E_d, eV	E_g, eV [11]	R_{ex}, eV [11]	E_0/E_g	ε_∞	ε_∞^* [17]	ε_0^* [17]
CdI_2	5.46	16.7	4.17	0.2	1.44	4.05	4.41	12.1
ZnI_2	6.38	15.7	4.62	0.16	1.36	3.46	—	—

with experimental dependence (Fig. 2). The E_0 and E_d values are listed in the Table. The ratio E_0/E_g indicated is near to 1.5. This value has been shown [14] to be typical of many materials. The value $E_0 = 5.46$ eV obtained for the polycrystal CdI_2 films is close to the corresponding value in crystals $E_{0\perp} = 5.8$ eV for s-polarisation ($\mathbf{E}_0\perp\mathbf{c}$) [10], thus confirming the texturing of films with an **c** axis perpendicular to the substrate.

According to [14], the oscillator energy E_0 is close to the spectral position of the absorption band maximum corresponding to interband transitions. For CdI_2, the obtained value $E_0 = 5.46$ eV is close to the spectral position of the electron band in absorption spectrum $E_m = 5.38$ eV [12] and is in agreement with the energy band structure calculation results for 4H polytype [16]. For ZnI_2, the value $E_0 = 6.38$ eV exceeds that for CdI_2 ($\Delta E_0 = 0.92$ eV), thus being in agreement with the value of the absorption edge shift in ZnI_2 with respect to direct transitions in CdI_2 ($\Delta E_g = 0.45$ eV [11]) (see Table).

Of interest is to compare the data on E_0 and E_d with the values measured for single crystals interest. It is established [10] that at the polarisation $\mathbf{E}_0\perp\mathbf{c}$ in CdI_2 $E_{0\perp} = 5.8$ eV and $E_{d\perp} = 23.1$ eV. In [14], the proportionality of E_d to the material density ρ was shown. The ratio of $E_{d\perp}/E_d$ in CdI_2 film is 0.725. The density reduction indicates the film porosity, as the specific volume occupied by pores $q = 1-\rho_f/\rho_{kr}$. Therefrom, $q = 0.272$. The high porosity should result in an appreciable light scattering in the film in a visible band, that is not observed in our experments. Let other data be considered concerning the refractive index measuring in CdI_2 single crystals. In [17], the optical constants were measured at $E_0\perp\mathbf{c}$ in the wavelength λ range including the band connected with excitation of TO phonons at $\hbar\omega_{TO} = 0.0075$ eV. At $\hbar\omega > \hbar\omega_{TO}$, the refractive index dispersion is absent in the CdI_2 transparence range and $n_\perp = 2.1$ at $\hbar\omega = 0.0375$ eV. An assessment of $n_\perp$ using our measurements and formula (4) gives $n_\perp =$

2.02 at the same $\hbar\omega$ value. Thus, the E_d value from the data [17] is 18.7 and is closer to $E_d = 16.7$ from our measurements in a film. Apparently the value $E_{d\perp}$ in [10] is overrated because of an error in determination of interference bands order m, originating in rather thick (~ 5 μm) single crystal plates. Nevertheless, the comparison with data [17] also indicates the film porosity, but at the same time $q\approx0.1$.

Approximating of formula (4) to a low-energy limit gives the optical dielectric constant value $\varepsilon_\infty = 1+E_d/E_0 = 4.05$ in CdI_2 and 3.46 in ZnI_2; it is an important constant used at analysis of the exciton spectra. The absorption exciton spectrum of CdI_2 and ZnI_2 thin films was investigated in [11, 18]. The parameters of long-wave exciton band in the spectra (the position E_m, the half-width Γ and ε_{2m} — the imaginary part value of permittivity in the band maximum) were determined by approximating it by a symmetrical mixed contour representing a linear combination of Lorentzian and Gaussian ones, using the method [19]. The exciton band parameters were selected such that the calculated contour and experimental dependence of optical density $D(E)$ were conformed in the best way on the band long-wave branch. After this band corresponding to the 1s exciton was subtracted, a new weaker band was observed adjasent to an edge of interband direct transitions and coresponding to excitation of the exciton with a main quantum number $n = 2$ (the 2s exciton). From the spectral positions of 1s and 2s bands, the exciton binding energy R_{ex} and the band-gap energy $E_g = E_m+R_{ex}$ is determined. Let the determination of E_g and R_{ex} for CdI_2 [11] be taken as an example.

Apparently (Fig. 4), the introduction of ions Zn into CdI_2 film in a low concentration ($x = 0.05$) changes cardinally the absorption spectrum of CdI_2: the absorption associated with the indirect transitions giving $E_g = 3.43$ eV at 80 K [8] disappears while the 1s exciton band X_1 appears at 3.97 eV. The weaker 2s exciton band X_1' is located at the short-wave side of this band at 4.12 eV. $R_{ex} = 0.2$ eV and the band-gap energy for direct transitions $E_g = 4.17$ eV
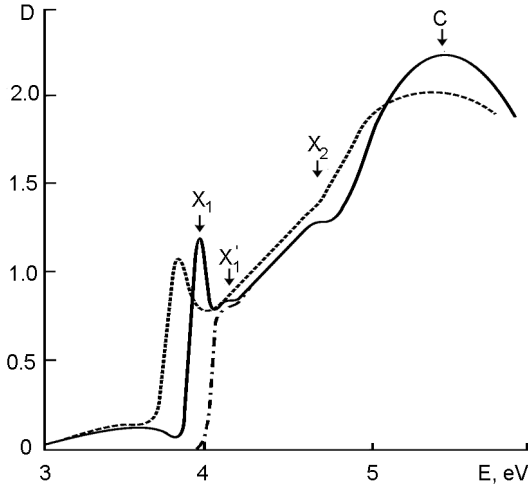
Fig. 4. Absorption spectra of CdI_2 activated with ions Zn ($x = 0.05$) at 290 K (dotted line) and 90 K (solid line), dash-and-dot line shows the absorption edge after separation of the X_1 band.

are determined basing on these data. The latter value agrees perfectly with theoretical evaluation of $E_g = 4.3$ eV at 30 K [7] for direct allowed transitions. A similar analysis of exciton bands in ZnI_2 in [11] gives $R_{ex} = 0.16$ eV and $E_g = 4.62$ eV (see Table). This analysis has been carried out using the model of Wannier-Mott excitons (large radius excitons). A number of the difficulties due to the crystal anisotropy and an the intermediate character of excitons between the Wannier-Mott ones and Frenkel excitons (small radius excitons) arises when studying the exciton states in layered crystals with large E_g and ionic character of interatomic bond.

When considering the anisotropy influence on the exciton spectrum of layered crystal, the parameter $\gamma = \varepsilon_\perp \mu_\perp / \varepsilon_\parallel \mu_\parallel$, is introduced taking into account the permittivity difference at E_0 perpendicular and parallel to **c** and reduced electron and hole masses $\mu_\perp$ and $\mu_\parallel$ [20]. At $\gamma \ll 1$, the excitons acquire two-dimensional (2D) character and are located in one layer. But at $\gamma \approx 1$, the model of 2D exciton will not be realized because of $\varepsilon_\perp > \varepsilon_\parallel$ and $\mu_\parallel > \mu_\perp$ and, as experiments have evidenced, the excitons show 3D character in many crystals. Besides, even at $\gamma < 1$, the anisotropy influences assessment R_{ex} and E_g only a little [11].

It follows from the above that it is necessary to assess the exciton radius a_{ex} to clear up the exciton states character in CdI_2 and ZnI_2. To calculate a_{ex}, let the data be used from [17] on energies $\hbar\omega_{TO} = 0.075$ eV

and $\hbar\omega_{LO} = 0.0124$ eV for transversal and longitudinal optical phonons at $E_0 \perp c$. The static dielectric permittivity ε_0 is calculated using these values and the known value ε_0:

$$\varepsilon_0 = \varepsilon_\infty \left(\frac{\omega_{LO}}{\omega_{TO}} \right) = 12.1. \tag{5}$$

Since the effective permittivity $\varepsilon_{eff} > \varepsilon_\infty$, but $\varepsilon_{eff} < \varepsilon_0$ for excitons of an intermediate coupling, then

$$a_{ex} = a_B \frac{R}{R_{ex}\varepsilon_{eff}}, \tag{6}$$

where $a_B = 0.529 \cdot 10^{-8}$ cm is the Bohr radius; $R = 13.6$ eV, the Rydberg constant; $R_{ex} = 0.2$ eV for CdI_2. The value ε_{eff} is unknown, therefore, let its extreme limits be used. At $\varepsilon_{eff} = \varepsilon_0$, we get $a_{ex} = 2.98 \cdot 10^{-8}$ cm, and at $\varepsilon_{eff} = \varepsilon_\infty$, $a_{ex} = 8.15 \cdot 10^{-8}$ cm. The first assessment is in a full inconsistency with the large radius exciton model, because for this model $a_{ex} > a_i$ of CdI_2 lattice parameters, while for Frenkel exciton, $a_{ex} < a_i$. The second assessment is more realistic, as $a_{ex} \approx a_i$ and we have excitons of an intermediate band for which ε_{eff} it is close to ε_∞. A similar calculation using formula (6) at $\varepsilon_{eff} = \varepsilon_\infty$ gives $a_{ex} = 12.9 \cdot 10^{-8}$ cm for ZnI_2.

4. Conclusion

The refractive index and its dispersion has been measured in thin CdI_2 and ZnI_2 films. It is shown that the spectral dependence $n(\lambda)$ consists with the monooscillatory Wemple model within the 300–1000 nm range. The $n(\lambda)$ data for CdI_2 are compared with data for single crystals obtained by other authors, and it is found that the CdI_2 films are textured with the texture axis being parallel to **c** axis and have a low porosity. The found parameters E_0 for the Wemple model are compared to theoretical calculations of the electron spectrum and measurements of the CdI_2 fundamental band spectrum. The band gap energy found from the measurings for direct allowed transitions (4.17 eV, 90 K) agrees well with theoretical calculations (4.3 eV). The optical permittivity is found also using the monooscillatory model parameters. The radius of $1s$ exciton in CdI_2 and ZnI_2 is calculated using the optical permittivity. It is shown that the excitons in these compounds belong to excitons of an intermediate bond.

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Дисперсія показника заломлення у тонких плівках CdI$_2$ та ZnI$_2$

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У тонких плівках CdI$_2$ та ZnI$_2$ виміряно дисперсію показника заломлення в інтервалі довжини хвиль 300–1000 нм, і одержані результати оброблено з застосуванням одноосциляторної моделі, яка добре узгоджується з експериментальними даними. За знайденими параметрами цієї моделі визначено оптичну діелектричну проникність ε_∞ обох сполук, яку використано для подальшого аналізу екситонних станів у CdI$_2$ та ZnI$_2$ і, зокрема, для визначення радіуса $1s$-екситонів. Знайдені значення a_{ex} є близькими до параметрів елементарної комірки сполук, що вказує на належність екситонів в обох сполуках до екситонів проміжного електрон-діркового зв'язку.