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Analysis of exciton reflection spectrum of 2H-PbI_2 layered single crystals with atomically clean surface

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Abstract. We performed the computer modelling of the dispersion dependences of real $\varepsilon_1(E)$ and imaginary $\varepsilon_2(E)$ parts of complex dielectric function $\varepsilon(E)$ for 2H-PbI_2 crystals with atomically clean surface at the temperature 5 K and the light polarization $\vec{E} \perp C$ and determined the energy position of the exciton bands and the parameters of the critical points. The obtained data allowed us to conclude the exciton spectra of this semiconductor can be described in terms of a single Wannier series with a large ground-state anomaly caused by a repulsive central-cell correction due to the cationic character of the exciton.

Keywords: quasi-surface and bulk excitons, computer modelling, optical functions, 2H-PbI_2 layered single crystals.

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1. Introduction

The quasi-surface excitons were found in exciton reflection spectra of both pure[1] and doped[2] with Mn and Cr impurities BiI_3 layered single crystals with atomically clean surface. It was interesting to look for quasi-surface excitons in another crystals, for example 2H-PbI_2.

On the other hand, in [3] proposed was the self-consistent method to divide the complicated contours of optical functions by separate components. Therefore, it was reasonably to use this method to analyze the optical spectra of 2H-PbI_2 substances.

The aim of the present work is to study exciton reflection spectra of 2H-PbI_2 layered single crystals with atomically clean surface.

2. Model description

The contribution of the damping factor Γ into dispersion dependence of $\varepsilon(E)$ is described by the equation [4]

$$\varepsilon(E,\Gamma) = 1 + \frac{e^2\hbar^2}{\pi^2 m^2 E^2} \int dE \int_S dk_1 dk_2 \frac{\left|\hat{\mathbf{e}} \cdot \mathbf{P}_{cv}(\mathbf{k})\right|^2}{\left|\nabla E_{cv}(\mathbf{k})\right|} \times \times \left[\frac{1}{E_{cv}(\mathbf{k}) - E - i\Gamma} + \frac{1}{E_{cv}(\mathbf{k}) + E + i\Gamma} \right], \quad (1)$$

where $\mathbf{P}_{cv}(\mathbf{k})$ is the matrix element of the electron transition from the top of the valence band v to the bottom of conduction band c; $E_{cv}(\mathbf{k}) = E_c(\mathbf{k}) - E_v(\mathbf{k})$ is the energy of the transition; k_1 and k_2 are variables that locate a point on the constant-energy surface S and which are determined from relation $E_{cv}(\mathbf{k}) = E$; m is the electron effective mass; $\hat{\mathbf{e}}$ is the unit polarization vector of the photon electric field; Γ is the phenomenological broadening parameter (damping constant).

As in the works [4-9], one can integrate the formula (1) having previously made the substitution $E_{cv}(\mathbf{k}) = E_j$, $\Gamma = \Gamma_j$ (j = 0,1,2,3,4 is the index of electron transition). Integrating gives the following expression for the complex dielectric function:

$$\varepsilon(\omega) = Ae^{i\Theta} F(z) . \quad (2)$$

Here

$$F(z) = \left[(f(1) - f(1+z)) + (f(1) - f(1-z)) \right] \frac{1}{z^2} , \quad (3)$$

$$f(z) = B \int_0^\infty z^{[D-4]/2} dz , \; B = \text{const} > 0, \quad (4)$$

$$z = \frac{E + i\Gamma_j}{E_j} = \frac{\hbar\omega + iG}{\hbar\Omega_0} . \quad (5)$$

$D = 0$ for the damping harmonic oscillator (DHO) and $D = 1,2,3$ for 1D, 2D, 3D types of critical points (CP), respectively; Θ is a phase angle for every type of CP ($\Theta = 0$ for M_0, $\Theta = \pi/2$ for M_1, $\Theta = \pi$ for M_2, $\Theta = 3\pi/2$ for M_3); Ω_0 is the resonance frequency of CP; G is a broadening; A is an amplitude.

An accuracy of the modelling can be significantly improved when using the adjustable broadening. Therefore, we replace the damping constant Γ_j for each transition j with the frequency-dependent expression $\Gamma_j(\hbar\omega)$ [8,9]

$$\Gamma_j(\hbar\omega) = \Gamma_j \exp\left[-\alpha_j\left(\frac{\hbar\omega - \hbar\Omega_0}{\Gamma_j}\right)^2\right] \qquad (6)$$

Varying parameter α_j from 0 to 0.3 the broadening function is changed from the Lorentzian ($\alpha_j = 0$) to the Gaussian broadening ($\alpha_j = 0.3$).

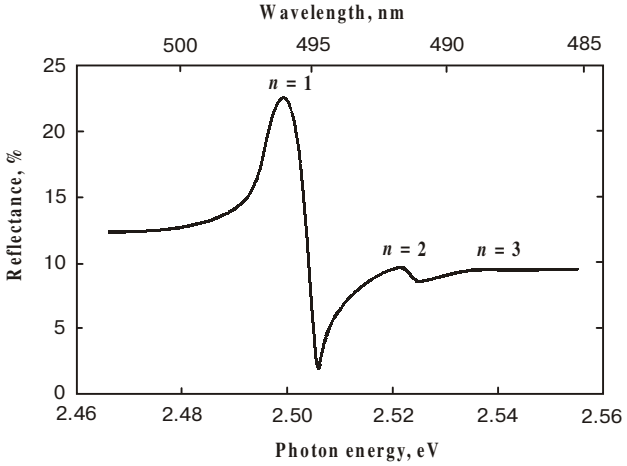

Fig. 1. The reflection spectrum of 2H-PbI_2 layered single crystals with atomically clean surface at $T = 5$ K and $\vec{E} \perp \vec{C}$.

3. Results and discussion

2H-PbI_2 layered single crystals were grown by the Bridgman method. The samples with dimensions 5×5×1 mm^3 were obtained by breaking off a bulk crystal with a blade. Special attention was paid to avoid the deformation. The atomically clean surface was obtained by taking off the layers with the scotch tape in cold helium vapor. The samples had the mirror smooth surface. The reflection spectra were registered with the photomultiplier FEU-100 on the automatic experimental setup based on MDR-23 monochromator with spectral resolution better than 0.5 meV.

The typical reflection spectrum of 2H-PbI_2 layered single crystals with atomically clean surface is shown in Fig. 1 at the temperature $T = 5$ K and light polarization $\vec{E} \perp \vec{C}$. The usual dispersion dependence $R(\lambda)$ with one high and two weaker oscillations, maxima of which are located at $\lambda = 4964$, 4920 and 4906 Å, accordingly, correspond to ground $n = 1$ and excited $n = 2$ and $n = 3$ states of the allowed direct excitons [10]. This indicates the quality of used crystals is high. It should be noticed also that none additional line or band was not observed in studied spectral range. Therefore, we can conclude that quasi-surface excitons in 2H-PbI_2 did not appear. The reason of this may be caused with higher exciton radius in this material ($r_{ex} \approx 20$ Å [10]) than in BiI_3 ($r_{ex} \approx 10$ Å [11]).

The real $\varepsilon_1(E)$ and imaginary $\varepsilon_2(E)$ parts of the complex dielectric function $\varepsilon(E)$ as a function of photon energy were calculated using the obtained reflection data and Kramers-Kronig relations. The expression (2) for DHO and all types of CP was used for their computer modelling taking into account the dispersion dependence of broadening function $\Gamma_j(\hbar\omega)$ (6). The computer program was written on Turbo Pascal 7.0.

The modelling process is based on the creation and approximation of number of models describing all type of CP for the dispersion dependence of ε_1 and ε_2. Each model corresponds to a definite type of Van Hove singularities [12]. The sum of model curves is compared then with the shape of ε_2 curve obtained from experimental data. It is necessary to convert ε_2 model curve via Kramers-Kronig relations into ε_1 one. The sum of curves obtained in such manner should be compared with the shape of experimental ε_1 curve. It should be emphasized that this procedure is simultaneously performed in the same program window. This gives the opportunity to control interactively the correspondence of real and imaginary parts of the model complex dielectric function with experimental ones.

Thus, varying the adjustable parameters of CPs one can properly approximate the shape of the ε_1 and ε_2 model characteristics.

The modelling results for ε_1 and ε_2 of 2H-PbI_2 are presented in Fig. 2. There are three clear exciton oscillations that put together the model dielectric function. The corrected spectral position of the bands and the numerical values of CP parameters for 2H-PbI_2 compounds are indicated in the table. The evaluations on the base of the obtained spectral positions of the bands show that the exciton spectra in 2H-PbI_2 can be described in terms of a single Wannier series with a large ground-state anomaly. This anomaly is explained by G.Harbeke and E.Tosatti [10] as a repulsive central-cell correction due to the cationic character of the exciton.

Table. Parameters of critical points and energy positions of exciton bands in optical functions of 2H-PbI_2 layered single crystals.

№	type of CP	$\hbar\Omega_0$, eV	A	G, meV	Θ, deg	α
CP1	DHO	2.501	2.99	3.0	5.0	0.01
CP2	DHO	2.523	0.34	4.7	–0.5	0.00
CP3	DHO	2.541	0.19	7.9	0.0	0.00

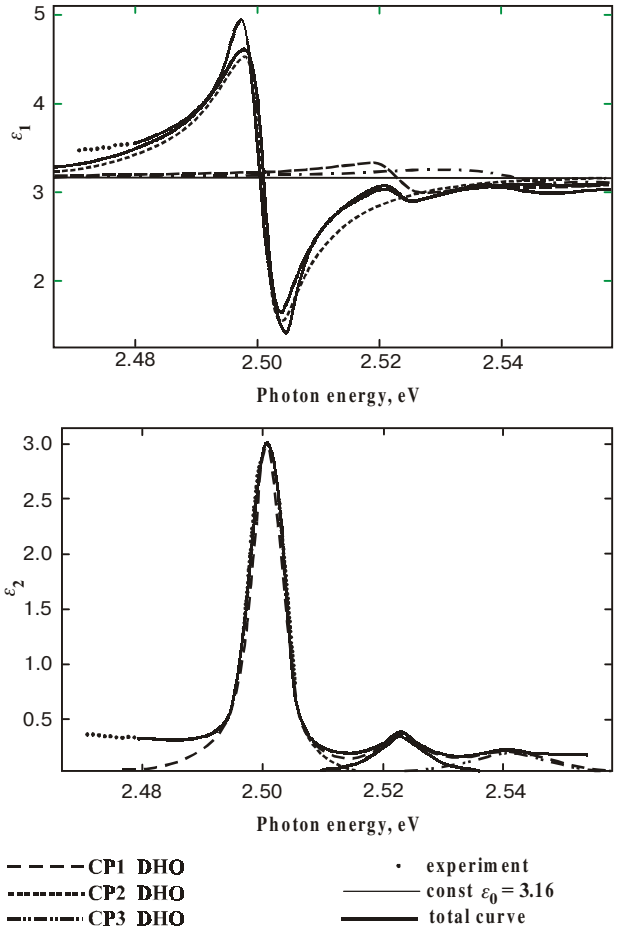

Fig. 2. Modelling of the real $\varepsilon_1(E)$ and imaginary $\varepsilon_2(E)$ parts of the complex dielectric function $\varepsilon(E)$ as a function of photon energy of 2H-PbI_2 layered single crystals with atomically clean surface at T = 5 K and $\vec{E} \perp \vec{C}$.

4. Conclusions

The exciton reflection spectra of 2H-PbI_2 single crystal with atomically clean surface were measured at the temperature 5 K and the light polarization $\vec{E} \perp \vec{C}$. The quasi-surface excitons were not found that may be caused with the higher exciton radius in this material than in BiI_3. The computer modelling of the dispersion dependences of real $\varepsilon_1(E)$ and imaginary $\varepsilon_2(E)$ parts of complex dielectric function $\varepsilon(E)$ for 2H-PbI_2 crysatals were performed. The energy position of the bands and the parameters of the critical points of the exciton reflection spectra were determined. It is shown that the exciton spectra in 2H-PbI_2 can be described in terms of a single Wannier series with a large ground-state anomaly caused by a repulsive central-cell correction due to the cationic character of the exciton.

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