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 $\varepsilon_r(E)$ and imaginary $\varepsilon_i(E)$ 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 $E \perp C$ 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 $\Gamma$ into dispersion dependence of $\varepsilon(E)$ is described by the equation [4]

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

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

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

$$\varepsilon(\omega) = A e^{i\Theta} F(z).$$

Here

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

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

$$z = \frac{E + i\Gamma_j}{E_j} = \frac{h\omega + iG}{h\Omega_0}.$$
\( D = 0 \) for the damping harmonic oscillator (DHO) and \( D = 1,2,3 \) for 1D, 2D, 3D types of critical points (CP), respectively; \( \Theta \) is a phase angle for every type of CP \( (\Theta = 0 \text{ for } M_0, \Theta = \pi/2 \text{ for } M_1, \Theta = \pi \text{ for } M_2, \Theta = 3\pi/2 \text{ for } M_3); \Omega_0 \) 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 \( \Gamma_j \) for each transition \( j \) with the frequency-dependent expression \( \Gamma_j(h\omega) \) \([8,9]\)

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

(6)

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

### 3. Results and discussion

2H-PbI\(_3\) layered single crystals were grown by the Bridgman method. The samples with dimensions 5x5x1 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\(_3\) layered single crystals with atomically clean surface is shown in Fig. 1 at the temperature \( T = 5 \) K and light polarization \( E \perp C \). 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\(_3\) did not appear. The reason of this may be caused with higher exciton radius in this material \( (r_{ex} = 20 \) Å \([10]\) than in BiI\(_3\) \( r_{ex} = 10 \) 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 \( \Gamma_j(h\omega) \) \( (6) \). 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 \( \varepsilon_1 \) and \( \varepsilon_2 \). Each model corresponds to a definite type of Van Hove singularities \([12]\). The sum of model curves is compared then with the shape of \( \varepsilon_2 \) curve obtained from experimental data. It is necessary to convert \( \varepsilon_2 \) model curve via Kramers-Kronig relations into \( \varepsilon_1 \) one. The sum of curves obtained in such manner should be compared with the shape of experimental \( \varepsilon_1 \) 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 \( \varepsilon_1 \) and \( \varepsilon_2 \) model characteristics.

The modelling results for \( \varepsilon_1 \) and \( \varepsilon_2 \) of 2H-PbI\(_3\) 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\(_3\) 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\(_3\) can be described in terms of a single Wannier series with a large ground-state anomaly. This anomaly is explained by G. Harbecke 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\(_3\) layered single crystals.

<table>
<thead>
<tr>
<th>#</th>
<th>type of CP</th>
<th>( h\Omega_0 , \text{eV} )</th>
<th>( A )</th>
<th>( G , \text{meV} )</th>
<th>( \Theta , \text{deg} )</th>
<th>( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP1</td>
<td>DHO</td>
<td>2.501</td>
<td>2.99</td>
<td>3.0</td>
<td>5.0</td>
<td>0.01</td>
</tr>
<tr>
<td>CP2</td>
<td>DHO</td>
<td>2.523</td>
<td>0.34</td>
<td>4.7</td>
<td>-0.5</td>
<td>0.00</td>
</tr>
<tr>
<td>CP3</td>
<td>DHO</td>
<td>2.541</td>
<td>0.19</td>
<td>7.9</td>
<td>0.0</td>
<td>0.00</td>
</tr>
</tbody>
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V.G. Dorogan et al.: Analysis of exciton reflection spectrum ...

higher exciton radius in this material than in BiI₃. The computer modelling of the dispersion dependences of real ϵ₁(E) and imaginary ϵ₂(E) parts of complex dielectric function ϵ(E) for 2H-PbI₂ crystals was 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-PbI₂ 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.

4. Conclusions

The exciton reflection spectra of 2H-PbI₂ single crystal with atomically clean surface were measured at the temperature 5 K and the light polarization $E \perp C$. The quasi-surface excitons were not found that may be caused with the

References

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