Temperature Behavior of Exciton Absorption Bands in PbJ_2 Layer Crystals

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Received 12.04.2002

Abstract

The influence of bending waves on the warm-up behavior of exciton absorption bands in layer crystals has been investigated. The effective mass of the current carriers in the layer semiconductor PbJ_2 has been computed and used to obtain the values of the exciton-phonon interaction function by pseudopotential method energy spectra calculations. It was shown that the different signs of the warm-up dynamics of an exciton absorption peak shift and existence of inversion points is related with the concurrent influence of two exciton energy relaxation mechanisms – on both the bending waves and the lattice phonons.

Keywords: layer crystal, lead iodide, exciton

PACS: 71.3S-y

Introduction

Layer semiconductors are unique crystal structures for studying mechanical and electrical properties of sharply anisotropic crystals by optical methods. The difference in quantities of intra- and interlayer interaction in layer crystals leads to anomalies in electronic and vibronic spectra. Sharp anisotropy of effective masses of the free carriers of charge and appearance of the low energy modes in vibronic spectra are the prime examples of the particularities of such crystals [1]. The low energy optical phonons and bending waves (the membrane type fluctuations of the layer packet) in the acoustic mode of vibronic spectra belong to this category. Optical spectra in the exciton range of frequencies clearly point to the influence of these factors on the mechanism of interaction of light with the layer crystals. This is manifested, in particular, by the essential difference of the warm-up shifts of an exciton band of the light absorption. First of all, the warm-up shifts of an exciton band in the layer crystal are observed in the range of low temperatures ($T<50$ K). They are not observed in isotropic crystals at these temperatures. Secondly, all the rest of the spectral features (bandwidth, symmetry, and absorption peak) are practically constant in this temperature range. Thirdly, the direction of displacement can be different in different layer crystals, while the short-wave offset of the absorption band in isotropic crystals is absent. The anomaly of the warm-up shifts of an exciton absorption band is explained by means of the banding waves model [2], the exciton-phonon interaction function V_2 can be both positive or negative, and related with the anisotropy of the effective mass of electron and hole: $V_2 \sim (m_e - m_h)$.

Hereupon, depending on the ratio of the charge carrier effective masses for certain directions of spreading light (parallel or perpendicular to the layer packet), different directions of changes in the position of the exciton energy level are possible. This mechanism of the relaxation of the light wave energy completely explains all available experimental data on the warm-up shift of an exciton absorption band in the layer crystals [3]. But sometimes the difference from experimental data was noted. For instance, the ratio of the charge carrier effective masses in PbJ_2 ($m_e^{\|} \approx m_h^{\|}$, $m_e^{\perp} << m_h^{\perp}$), stated in [4], indicates the absence or weak exciton-phonon interaction when the direction of spreading light is parallel to the layer plan, and strong in the perpendicular direction. At the same time, the behavior of the shifts of exciton line is practically the same for different geometries of the experiment [5]. Besides there essential scattered data exists on the quantities of the charge carrier effective masses, measured for the same crystals by different authors.

The aim of this investigation is to calculate the values of the effective masses of electron and hole in a concrete type of layer crystal on the base of the energy spectrum of its electronic system, and to determine the warm-up genesis of the form of the exciton absorption band, as well as the warm-up shift of its peak for several geometries of the experiment. As an example, the PbJ_2 layer semiconductor has been chosen because there are numerous experimental data of its optical absorption spectra.

Form of the exciton absorption band

Coefficient K of the absorption of light with a frequency ω is defined [6] by the exciton with energy E_0 as an imaginary part of the lagging of Green's function:

$$K(\omega) = D_0 \frac{\Gamma(\omega)}{[\omega - E_0 - \Delta(\omega)]^2 + \Gamma^2(\omega)}, \quad (1)$$

where D_0 - parameter of the exciton-photon interaction, and $\Delta(\omega) + i\Gamma(\omega) = M(\omega)$ - mass operator of excitons, the magnitude of which completely depends on exciton energy relaxation and, in particular, on the character of exciton-phonon interaction.

When considering the dissipation mechanisms of exciton energy in layer crystals, the nonlinear exciton-phonon interaction as well as the traditional linear interaction should be taken into account. This is connected with the peculiarity of the layer crystal structure, which can be visualized as a set of the layer packet strings on the axis c that is perpendicular to the packet plane. Every layer packet consists of one or a few atom planes (for instance in PbJ_2 there are J–Pb–J). The interaction between the atoms inside the layer is strong but the interlayer interaction is weak. So when considering the springy characteristics of such structures it is necessary to take into account the possibility of the deformation effects of the layer packet bending. This very fact predetermines the appearance of an additional type of acoustic vibrations - bending waves with square-law dispersions. Furthermore, the deformation potential, which describes the interaction of charge carriers with the lattice vibrations in the semiconductor, must take into consideration the volume change caused not only by the springy deformation of the lattice, but also by the deformation of the layer bending. Since the latter leads to a volume change only in the square-law on the atom displacement approach, the interaction between excitons and bending waves must be described already by nonlinear term on phonons [7]:

$$\begin{aligned} V = &\sum_{\vec{k},\vec{q}} V_1(\vec{q}) a^{+}_{\vec{k}+\vec{q}} a_{\vec{k}} \varphi_{\vec{q}} + \\ &+ \sum_{\vec{k}_1 \vec{q}_1 \vec{q}_2} V_2(\vec{q}_1, \vec{q}_2) a^{+}_{\vec{k}+\vec{q}_1+\vec{q}_2} a_{\vec{k}} \varphi_{\vec{q}_1} \varphi_{\vec{q}_2} \end{aligned} . \quad (2)$$

The first term in (2) describes the exciton-phonon interaction, which is linear in respect to the phonon operators, and the second one – a nonlinear interaction of excitons with the bending waves, where V_1 and V_2 are the functions of excitons connection with the phonon of corresponding branch of the lattice vibration spectra, $a^{+}_{\vec{k}}$ and $a_{\vec{k}}$ - creation and destroying operators of exciton with wave vector $\vec{k}$ and energy $E_{\vec{k}}, \varphi_{\vec{q}} = b_{\vec{q}} + b^{+}_{-\vec{q}}$, where $b^{+}_{\vec{q}}$ and $b_{\vec{q}}$ - creation and destroying operators of phonons in state $\vec{q}$ with energy $\Omega_{\vec{q}}$.

If both mechanisms of energy relaxation are considered, the mass operator of excitons can be written as [8]:

$$M(\omega,T) = M_1(\omega,T) + M_2(T), \qquad (3)$$

where

$$M_1(\omega,T) = \sum_{\vec{q}} V_1^2(\vec{q}) \times$$

$$\times \left(\frac{n_{\vec{q}}}{\omega - E_{\vec{k}} - M_2(\vec{q}) + \Omega_{\vec{q}} + i\eta} + \right. \qquad (4)$$

$$\left. + \frac{1 + n_{\vec{q}}}{\omega - E_{\vec{k}} - M_2(\vec{q}) - \Omega_{\vec{q}} + i\eta} \right)$$

$$M_2(T) = \sum_{\vec{q}} V_2(\vec{q},-\vec{q})(1 + 2n_{\vec{q}}) \qquad (5)$$

- terms, caused, correspondingly, by the linear and nonlinear exciton-phonon interaction. Here $n_{\vec{q}} = [\exp(\Omega_{\vec{q}} / k_B T) - 1]^{-1}$ - completing numbers of the phonon states at the temperature *T*, k_B – Boltzmann's constant. As it follows from (5), damping of the exciton excitation is caused only by linear exciton-phonon interaction, while the square-law mechanism of relaxation predetermines an additional shift of the exciton absorption band. Herewith the direction of this shift depends completely on the sign of the function of nonlinear exciton-phonon interaction, and, thus can intensify the linear shifts mechanism in one case, or level it in the other.

Calculation of the effective masses

Magnitudes of effective masses of the free carriers of charge in PbJ_2 were calculated on the base of one-electron energy spectrum calculation, as the components of the inverse effective masses tensor

$$\frac{1}{m_{\alpha\beta}} = \frac{1}{\hbar^2} \frac{\partial^2 E_n(\vec{k}_0)}{\partial k_\alpha \partial k_\beta} \qquad (6)$$

are defined as the second derivative of the energies $E_n(\vec{k})$ of electron state with respect to components of vector state $\vec{k} = (k_x, k_y, k_z)$ in the extreme point $\vec{k}_0$. In the system of coordinates of the main axes of the crystals where Oz || *c*, we have:

$$\frac{1}{m^{\parallel}} = \frac{1}{\hbar^2} \frac{\partial^2 E_n(\vec{k}_0)}{\partial^2 k_z},$$

$$\qquad (7)$$

$$\frac{1}{m^{\perp}} = \frac{1}{\hbar^2} \left(\frac{\partial^2 E_n(\vec{k}_0)}{\partial^2 k_x} + \frac{\partial^2 E_n(\vec{k}_0)}{\partial^2 k_y} \right).$$

The dispersion law of electrons has been calculated by the pseudopotential method using an '*ab initio'* nonsingular pseudopotential [9]. If the spin-orbit interaction is not taken into account, it should be written as:

$$V_{ps}^{ion}(\vec{r}) = \sum_l |l\rangle V_l^{ion}(\vec{r}) \langle l| =$$

$$= \sum_l |l\rangle \left(V_{core}(\vec{r}) + \Delta V_l^{ion}(\vec{r}) \right) \langle l|, \qquad (8)$$

where

$$V_{core}(\vec{r}) = -\frac{Z_v}{r} \left| \sum_{i=1}^{2} C_i^{core} erf(\sqrt{\alpha_i^{core}}\, r) \right| \qquad (9)$$

- is a long-range Coulomb (*l*-independent) and

$$\Delta V_l^{ion}(\vec{r}) = \sum_{i=1}^{3} \left(A_i + r^2 A_{i+3} \right) \cdot \exp(-\alpha_i r^2) \quad (10)$$

- short-range (*l*-dependent) parts of ion pseudopotential, parameters of which have been calculated for majority elements in [9].

The energies of zone states $E_n(\vec{k})$ can be obtained as the eigenvalues of the pseudohamiltonian

$$H_{ps}(\vec{r}) = -\frac{\hbar^2 \nabla^2}{2m} + V_{ps}(\vec{r}), \qquad (11)$$

that are defined by the system of pseudowave functions $|\varphi_{n\vec{k}}> \equiv \sum_{\vec{g}} a_n(\vec{g}) | \vec{k} - \vec{g} >$ as a solution of

$$\det \left\| \left[\frac{\hbar^2}{2m}(\vec{k} - \vec{g}')^2 - E_n(\vec{k})\right] \delta_{\vec{g}',\vec{g}} + \left\langle \vec{k} - \vec{g}' \middle| V_{ps} \middle| \vec{k} - \vec{g} \right\rangle \right\| = 0.$$

Here $\left\langle \vec{k} - \vec{g}' \middle| V_{ps} \middle| \vec{k} - \vec{g} \right\rangle = V_L(q) + V_{NL}(\vec{K}, \vec{K}')$ is a matrix element of pseudopotential $V_{ps}(\vec{r})$, defined on the basis of normalized crystal volume Ω plane waves $|\vec{k}-\vec{g}>$, $V_L(q)$ and $V_{NL}(\vec{K},\vec{K}')$ - its local and, accordingly, nonlocal parts [10], $\vec{g}$ - reciprocal lattice vector, $q=|\vec{g}'-\vec{g}|$ and $\vec{K}=\vec{k}-\vec{g}$.

We obtained the pseudopotential (8) – (10) form factors for Pb and J in the case $q\cdot K\cdot K'\neq 0$ in analytical form:

$$v_L(q)=\frac{1}{\Omega_a}[-4\pi Z_v\sum_{i=1}^{2}\frac{C_i^{core}}{q^2}e^{-\frac{q^2}{4\alpha_i^{core}}}+$$

$$\sqrt{\pi^3}\sum_{i=1}^{3}(\frac{A_i}{\alpha_i^{3/2}}+\frac{A_{i+3}}{\alpha_i^{5/2}}(3-\frac{q^2}{2\alpha_i}))e^{-\frac{q^2}{\alpha_i}}],$$

$$v_{NL}(\vec{K},\vec{K}')=\frac{3\sqrt{\pi^3}\cos\theta}{\Omega_a}\times$$

$$\begin{aligned}\times\Bigg\{\Bigg[\sum_{i=1}^{3}\frac{A_i}{\sqrt{KK'}\alpha_i}\cdot I_{3/2}(K,K')\cdot e^{-\frac{K^2+K'^2}{4\alpha_i}}&+\\ +A_{i+3}\times\Bigg(\frac{J_1(K-K')-J_1(K+K')}{(KK')^2}&+\\ +\frac{J_2(K-K')+J_2(K+K')}{KK'}&-\\ -\frac{J_3(K-K')+J_3(K+K')}{K^2K'}&+\\ \frac{J_3(K-K')-J_3(K+K')}{K'^2K}\Bigg)\Bigg]_{l=1}-[\ldots]_{l=0}\Bigg\}&,\end{aligned}$$

where θ is the angle between the vectors $\vec{g}$ and $\vec{g}'$, $I_{3/2}(z)$ is a spherical Bessel function and

$$J_1(z)=\frac{1}{\sqrt{\alpha_i}}\cdot\exp(-\frac{z^2}{4\alpha_i}),$$

$$J_2(z)=\frac{2\alpha_i-z^2}{4\alpha_i^{5/2}}\cdot\exp(-\frac{z^2}{4\alpha_i}),$$

$$J_3(z)=\frac{z}{2\alpha_i^{3/2}}\cdot\exp(-\frac{z^2}{4\alpha_i}).$$

Nonscreening “bare” ions pseudopotential

$$\left\langle\vec{k}-\vec{g}'\middle|V_{ps}^{b}\middle|\vec{k}-\vec{g}\right\rangle=\sum_{\alpha}S_\alpha(\vec{g}-\vec{g}')\times$$

$$\times[v_L^\alpha(q)+v_{NL}^\alpha(\vec{K},\vec{K}')]\qquad(12)$$

allows to calculate zone state energies without considering the screening effects and exchange-correlation interactions. Where

$$S_\alpha(\vec{g}-\vec{g}')=N_\alpha^{-1}\sum_j e^{-i(\vec{g}-\vec{g}',\vec{\tau}_j)}$$

is a lattice structure factor (j is a number of α-species atoms of positions which are defined inside the unit cell by vector $\vec{\tau}_j$; N_α is a quantity of them).

Within of the linear screening theory in approach of local density of charge to (12) we must add the Fourier transformation of Hartree potential

$$V_H(\vec{g})=\frac{4\pi\in^2}{g^2}\rho(\vec{g}),\qquad(13)$$

and the exchange-correlation interaction can be described by introducing the appropriate potential, for example in X_α approximation [11]:

$$V_{xc}^\alpha(\vec{r})=\alpha V_x^s(\vec{r}).\qquad(14)$$

Where

$$V_x^S(\vec{r})=-\frac{3\in^2}{2}\left(\frac{3\rho(\vec{r})}{\pi}\right)^{1/3}\qquad(15)$$

is a Slater form of exchange potential, $\rho(\vec{g})$ is a Fourier transformation of ‘pseudocharge’ density $\rho(\vec{r})=2\sum_{n,\vec{k}}|\varphi_{n\vec{k}}(\vec{r})|^2$ (summation is over all occupied zones n and states $\vec{k}$ of the Brillouin zone), α is a parameter, the magnitude of which lies in the interval from 0.7 to 1, $\in^2=\frac{e^2}{4\pi\varepsilon_0}$.

In the first order of the perturbation theory on the basis of plane waves

$$|\varphi_{n\vec{k}}>=a_{n\vec{k}}(0)|\vec{k}>+\sum_{\vec{g}\neq 0}a_{n\vec{k}}(\vec{g})|\vec{k}-\vec{g}>,$$

where $a_{n\vec{k}}(0)$ and

$a_{n\vec{k}}(\vec{g}) = \dfrac{\left\langle \vec{k}-\vec{g}\middle|V_{ps}\middle|\vec{k}\right\rangle}{T_{\vec{k}} - T_{\vec{k}-\vec{g}}} a_{n\vec{k}}(0), (\vec{g} \neq 0)$ are the terms of zero or first order, respectively, and $T_{\vec{k}} = \hbar^2 k^2/2m$ - free electron energy ($T_{\vec{k}} \neq T_{\vec{k}-\vec{g}}$). Then for the term of the first order upon the magnitude of $\left\langle \vec{k}-\vec{g}\middle|V_{ps}\middle|\vec{k}\right\rangle$ - (13) will be as follows:

$$V_H(\vec{g}) = \frac{16\pi \in^2}{g^2\Omega} \times$$
$$\times \sum_{n,\vec{k}} \left|a_{n\vec{k}}(0)\right|^2 \frac{\left\langle \vec{k}-\vec{g}\middle|V_{ps}\middle|\vec{k}\right\rangle}{T_{\vec{k}} - T_{\vec{k}-\vec{g}}}. \qquad (16)$$

According to pseudopotential weakness we can expect that $a_{n\vec{k}}(\vec{g}) < a_{n\vec{k}}(0)$ when $\vec{g} \neq 0$. This allows to find

$$V_x^S(\vec{g}) = -\frac{\sqrt[3]{6} \in^2}{\sqrt[3]{\pi\Omega}[\sum_{n,\vec{k}} |a_{n\vec{k}}(0)|^2]^{2/3}} \times$$
$$\times \sum_{n,\vec{k}} \left|a_{n\vec{k}}(0)\right|^2 \frac{\left\langle \vec{k}-\vec{g}\middle|V_{ps}\middle|\vec{k}\right\rangle}{T_{\vec{k}} - T_{\vec{k}-\vec{g}}}. \qquad (17)$$

So pseudopotential is defined as a solution of the equation

$$\left\langle \vec{K}'\middle|V_{ps}\middle|\vec{K}\right\rangle = \left\langle \vec{K}'\middle|V_{ps}^b\middle|\vec{K}\right\rangle +$$
$$+\left(\frac{16\pi}{q^2\Omega} - \frac{\sqrt[3]{6}}{\sqrt[3]{\pi\Omega}[\sum_{n,\vec{k}} |a_{n\vec{k}}(0)|^2]^{2/3}}\right) \times$$
$$\times \sum_{n,\vec{k}} \left|a_{n\vec{k}}(0)\right|^2 \frac{\left\langle \vec{K}'\middle|V_{ps}\middle|\vec{K}\right\rangle}{T_{\vec{K}} - T_{\vec{K}'}} \qquad (18)$$

self-consistent over the magnitude of $\sum_{n,\vec{k}} \left|a_{n\vec{k}}(0)\right|^2$ with null approximation $\left\langle \vec{K}'\middle|V_{ps}\middle|\vec{K}\right\rangle^{(0)} = \left\langle \vec{K}'\middle|V_{ps}^b\middle|\vec{K}\right\rangle$. Values $a_{n\vec{k}}(0)$ will be computed in every point $\vec{k}$ on every step of the iterative procedure of searching for the solution of a secular equation, which includes them as components of corresponding eigenvectors of the one-electron pseudohamiltonians, which are defined in the plane wave basis.

On the ground of the energy spectrum, obtained in this way, calculations of components of the inverse effective mass tensor have been made, which are defined as partial derivatives of vector $grad_{\vec{k}} E_n(\vec{k})$ in respect to Cartesian coordinates of $\vec{k}$. But $grad_{\vec{k}} E_n(\vec{k}) = \hbar \vec{u}_n(\vec{k})$, where $\vec{u}_n(\vec{k})$ is the velocity of the electron, which is in the state $\vec{k}$ of zone *n*:

$$\vec{u}_n(\vec{k}) = \int \psi_{n\vec{k}}^*(\vec{r}) \frac{\hbar}{im_0} \nabla_{\vec{k}} \psi_{n\vec{k}}(\vec{r}) d^3\vec{r}.$$

On the basis of plan waves [12]

$$\vec{u}_n(\vec{k}) = \frac{\hbar}{m_0} \sum_{\vec{g}} |a_{n\vec{k}}(\vec{g})|^2 (\vec{k} - \vec{g}), \qquad (19)$$

so

$$\frac{\partial^2 E_n(\vec{k})}{\partial k_\alpha \partial k_\beta} = \frac{\hbar^2}{m_0} \sum_{\vec{g}} \{|a_{n\vec{k}}(\vec{g})|^2 \delta_{\alpha\beta} +$$
$$+ (k_\alpha - g_\alpha) \frac{\partial}{\partial k_\beta} |a_{n\vec{k}}(\vec{g})|^2\}, \qquad (20)$$

where m_0 is the mass of free electron. For plan waves

$$\sum_{\vec{g}} |a_{n\vec{k}}(\vec{g})|^2 = 1, \qquad (21)$$

So, definitely

$$\frac{1}{m_{\alpha\beta}} = \frac{1}{m_0} \{\delta_{\alpha\beta} +$$
$$+ \sum_{\vec{g}} (k_\alpha - g_\alpha) \frac{\partial}{\partial k_\beta} |a_{n\vec{k}}(\vec{g})|^2\}. \qquad (22)$$

Pseudopotential [9] is a norm-conserving one, so requirement (21) is execute for pseudowave functions. Thus we can use (22) for the calculation of the effective masses, if $a_{n\vec{k}}(\vec{g})$ is the meaning of components of accordant eigenvectors of the pseudohamiltonian (18). Derivatives in (22) were received by numerical methods but summation over $\vec{k}$-states in Brillouin zone has been realized by a special point scheme [13], used as that a set of points $\{(0,0,\frac{1}{4}),(\frac{1}{3},0,\frac{1}{4}),(\frac{1}{3},0,\frac{\overline{1}}{4}),(\frac{1}{3},\frac{1}{3},\frac{1}{4}),(\frac{1}{3},\frac{1}{3},\frac{\overline{1}}{4})\}$ from the irreducible part of the zone with the weighting factors $w_i=\{\frac{1}{9},\frac{1}{3},\frac{1}{3},\frac{1}{9},\frac{1}{9}\}$.

The calculated energy spectrum is in agreement with data obtained by empirical pseudopotential [14] and by LCAO [15] methods. Table 1 presents a list of effective masses of the electron and hole together with data on measurements [15]. As the matching shows, calculated magnitudes of effective masses are essentially relatively lower than experimental data but noted in [7] relations are executed, there is also sharp anisotropy of electron effective mass.

Table 1. Calculated and experimentally obtained values (in brackets) [4] of effective masses of the electron and a hole.

$m_e^{\parallel}/m_0$	$m_e^{\perp}/m_0$	$m_h^{\parallel}/m_0$	$m_h^{\perp}/m_0$
1,12 (1,25)	0,18 (0,25)	0,22 (1,1)	0,46 (1,1)

The excitons peak position in PbJ$_2$

For investigation of the spectral feature of the exciton absorption band we consider a layer semiconductor with covalent bonds between the atoms inside the layer packet where three-dimensional exciton with square-law dispersion is realized:

$$E(y)=E_0+Ly^2. \qquad (23)$$

Here $L=\pi/(2am_{ex})$ is a width of the exciton energy zone, $y=aq/\pi$ – dimensionless quasi-momenta of excitons whose mass is $m_{ex}=m_e+m_h$, and a – lattice constant. Lets take into consideration two mechanisms of the exciton relaxation: interaction with optical phonons whose dispersion law is $\Omega_y=\Omega_1$ and with bending waves for which $\Omega_y=\Omega_2 y^2$. The first interaction is linear over phonons with an exiton-phonon connection function

$$V_1^2(y)=F_0\Omega_1\left[\frac{1-\alpha_e y^2}{(1+\alpha_e y^2)^2}-\frac{1-\alpha_h y^2}{(1+\alpha_h y^2)^2}\right]^2$$

$$\equiv F_0\Omega_1F_1(y), \qquad (24)$$

and the second is nonlinear, with a connection function

$$V_2(y,-y)=\pm f_0\Omega_2 m_0\left(\frac{1}{m_e(1+\alpha_e y^2)^2}-\right.$$

$$\left.-\frac{1}{m_h(1+\alpha_h y^2)^2}\right)y\equiv f_0\Omega_2F_2(y)y. \qquad (25)$$

Here F_0 and f_0 are the factors of linear and nonlinear exciton-phonon interactions, respectively

$$\alpha_i=\left(\frac{\pi a_{ex}m_i}{2am_{ex}}\right)^2(i=e,h), \qquad a_{ex}=\frac{\varepsilon\, m_{ex}}{2m_e m_h},$$

and ε is a dielectric constant of the crystal; the plus sign in (25) corresponds to the parallel direction of spreading light, minus – to the perpendicular. Having made the transition in (4, 5) from the amount over $\vec{q}$ to integral over Brillouin zone in cylindrical coordinates, we have got the form of dependency from frequency and temperature the real

$$\Delta(\omega,T)=\Delta_1(\omega,T)+\Delta_2(\omega,T) \qquad (26)$$

and imaginary

$$\Gamma(\omega,T)=\Gamma_0+\frac{\pi}{2}F_0\Omega_1[F_1(q_+)n_1+$$

$$+F_1(q_-)(1+n_1)] \qquad (27)$$

parts of the mass operator (3), where

$$\Delta_2\equiv f_0\Omega_2\int_0^1[1+2n_2(y)]F_2(y)y^2dy,$$

$q_\pm=\sqrt{w-M_2(T)\pm\Omega_1}$, Γ_0 is the radiation width of exciton level, $w=(\omega-E_0)/L$, and $I(A)\equiv\int_0^1\frac{F_1(y)ydy}{A-E_0-\Delta_2-Ly^2}$ is the principal value of the integral.

The analysis of spectral and warm-up dependences of absorption bands for both directions of light spreading in crystal PbJ$_2$ has been realized by numerical methods. Calculated magnitudes of effective masses and the following parameters have been used for this:

Ω_1 = 120 см$^{-1}$, Ω_2 = 60 см$^{-1}$, $F_0^{\|} = 0{,}35$, $f_0^{\|} = 0{,}0002$, Γ_0 = 4,5 см$^{-1}$, ε = 11,1 and lattice parameters $a^{\|}$ = 4,557 Å, $a^{\perp}$ = 9,697 Å. The results show, that the temperature increase leads to expansion of the absorption band and reduces the height of its peak (Fig. 1), but the beginning of the change of these parameters corresponds to the range T > 40 K that was observed in isotropic crystals as well.

Quite a different situation is observed for the warm-up dependence of the position of exciton absorption peak. Because of the monotonicity of function $\Gamma(\omega)$ near the bottom of the exciton zone the position of the maximum of function (1) on the frequency scale can be defined as a solution of equation

$$\omega_m(T) = E_0 - \Delta_1(\omega_m, T) - \Delta_2(T). \quad (28)$$

In general, the position of the maximum and its warm-up dependence are defined by two mechanisms of exiton relaxation: by the linear interaction with optical phonons (Δ_1) and by nonlinear interaction with bending waves (Δ_2). Function $\Delta_1(\omega_m, T)$ was examined in detail experimentally and theoretically and has the following character: position of the maximum of the absorption band under low temperature is invariable, but within the high-temperature region (T> 60 K) there is a linear displacement with the temperature increasing to a long wave spectral range as a rule. In the case of exciton scattering on bending waves displacement appears in the low temperature (T<40 K) region as well. Direction of this displacement is defined only by the sign of the connection function V_2, which, as is shown in (25), is different for various directions in a crystal and, furthermore, depends on the ratio of effective mass magnitudes in the present layer crystal.

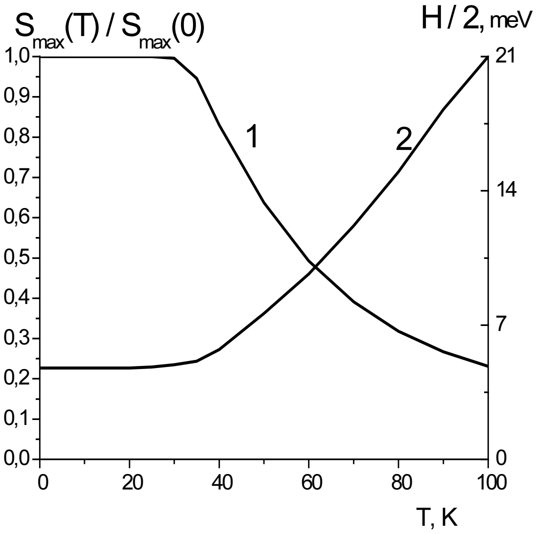

Fig.1. Warm-up dependencies of the normalized value of maximum (1) and half width H(T)/2 (2) of exciton absorption band in PbJ_2.

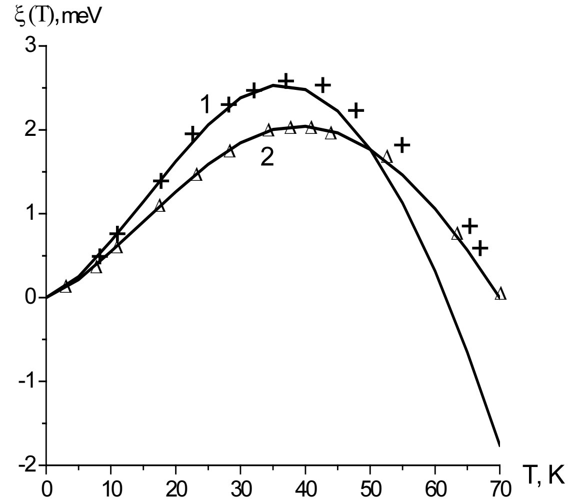

Fig. 2. Warm-up dependencies of calculated (solid lines) and measured in [5] (+ and Δ) magnitudes of the shifts of exciton absorption band peak for different directions of light spreading: in the plane of the layer packet (1) and perpendicular to it (2).

Obviously the real warm-up dependence of the position of the exciton absorption peak is defined by competition of both noted mechanisms of relaxation that leads to a nonmonotone behavior of function $\omega_m(T)$ and the appearance of extreme point. Temperature dependence of value $\xi(T) = \omega_m(T) - \omega_m(0)$ of the shifts increment of the exciton absorption band in different crystallographic directions in the PbJ_2 are shown in Fig. 2. For the calculation of the magnitudes $\xi(T)$ we have used values of effective masses obtained by us and fitting the experimental data [5] parameters of exciton-phonon interaction $F_0^{\|} = 3{,}2$, $f_0^{\|} = 0{,}0033$, $F_0^{\perp} = 9{,}1$ $f_0^{\perp} = 0{,}004$.

Conclusions

The behavior of the calculated and measured warm-up dependences of the shift of exciton absorption bands (Fig. 2) is proved by following:

– ‘*ab initio*’ calculations of the magnitudes of effective masses of free curriers of charge in PbJ_2 allows to describe quantitatively the warm-up behavior of excitons absorption bands more exactly, than the results of [4];

– warm-up genesis of exciton bands in the range of low temperatures is stipulated by the mechanism of relaxation of the exciton energy on the bending waves, but at higher temperatures – by relaxation on the lattice phonons;

– the same shifts of the exciton bands in the short wave spectra region in different geometries of experiment [5] are connected with the scattering of excitons on the bending waves for which, on the one hand, the exciton-phonon connection function (25) has opposite signs ($V_2^{\|} > 0$, $V_2^{\perp} < 0$), but on the other hand, the inequalities of the opposite signs are realized for magnitudes of effective masses of electron and hole, and thus $F_2^{\|} < 0$ since $m_e^{\|} > m_h^{\|}$, but $F_2^{\perp} > 0$ because $m_e^{\perp} < m_h^{\perp}$. In general this leads to the same directions of the shift: $V_2^{\|} < 0$, $V_2^{\perp} < 0$;

– factors of warm-up shift greatly depend on the direction: $d\xi^{\|}/dT >> d\xi^{\perp}/dT$. This fact demonstrates the anisotropy of exciton scattering on phonons and is defined both by anisotropy of effective masses and by difference of the spring properties of the crystal;

– comparison of angles of the slopping in dependency $\xi(T)$ indicates that in the range of low temperature excitons scattering over bending waves is more effective in the plane of the layer packet because of the great difference of effective masses ($m_e^{\|} >> m_h^{\|}$, $f_0^{\|} \leq f_0^{\perp}$), while at higher temperatures more effective scattering over the lattice phonons in the same direction is explained by the difference of exciton-phonon interaction parameters ($m_e^{\perp} \leq m_h^{\perp}$, $F_0^{\perp} >> F_0^{\|}$).

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