ANALYSIS OF ABSORPTION SPECTRA OF Bi-DOPED β-CdP_2 CRYSTALS

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Dependences of the variation of the single-photon absorption coefficient ΔK in a sensing wave on the Bi-doping degree as well as on the frequency and intensity of a pump wave have been investigated for the β-CdP_2 compound. The spectra obtained for Bi-doped crystals are much more complicated than those for undoped specimens. The schemes of the impurity energy levels in the valence (v) and conduction (c) bands and of the electron transitions have been built. A spectral band with the maximum at 1.30 eV induced by transitions between impurities and a band at 1.17 eV corresponding to the absorption of a phonon with an energy of 30 meV have been discovered.

Introduction

Semiconductor CdP_2 of the tetragonal modification (β) is a perspective compound for applied nonlinear optics, quantum electronics, and optoelectronics. Nevertheless, any application of the semiconductor requires knowing its physical and physical-chemical properties in detail. Therefore, the study of the band structure features and the impurity center parameters is one of the most urgent tasks of the spectroscopic investigations both in theoretical and application aspects. In this case, the development of new efficient methods of investigation is also needed. From this point of view, the amplitude and polarization laser-modulation spectroscopy is of special interest [1]. The investigations carried out by this method [1] showed that the absorption spectra of a sensing wave $\hbar\omega_2$ in Bi-doped specimens are mostly affected by a pump wave $\hbar\omega_1$. One of the reasons of such an effect of the Bi-doping on the laser-modulation spectra is the inversion of the conductivity type at doping, namely, from p-type (undoped crystals) to n-type (Bi-doped ones). This made it possible to discover four singularity points of the M_0-type in the electron density of quantum-mechanical states, one singularity point of the M_3-type in the conduction band, one point of the M_0-type in the valence band, and eight deep levels in the energy gap. Substantial variations in the nonlinear-spectroscopy spectra of the crystals are due to the presence of a Bi impurity and cannot be explained only by the inversion of a conductivity type at the Bi-doping. So, the problem of revealing other mechanisms of this phenomenon is challenging.

1. Objects and Methods of Investigations

We studied the Bi-doped β-CdP_2 single crystals of the tetragonal modification. The crystals were doped during their growth by admixing the dopant into initial components taken in the stoichiometric proportion. The conductivity type was determined according to the sign of the Hall electromotive force. The undoped specimens were of the p-type, while the specimens Bi-doped to 0.5 or 1% (hereafter, the weight concentration is quoted) were of the n-type. The width of the specimens transmitted both by the sensing and pump waves was $d = 1.4$ mm.

We studied the singularities, which are typical of the changes induced by the pump wave in the impurity absorption of the sensing one [1],

$$\Delta K_l^{(1)}(\omega_2) = K_l^{(1)}(\omega_2) - K_{0l}^{(1)}(\omega_2), \qquad (1)$$

where $K_{0l}^{(1)}(\omega_2)$ and $K_l^{(1)}(\omega_2)$ are the coefficients of the single-photon absorption resulting from electron and hole transitions between the separate impurity states l and the energy bands v and c of the crystal at the ignition time ($t = 0$) and at $t > 0$, respectively. If, under the direct influence of the pump wave, the population of the impurity states l changes, the value of $\Delta K_l^{(1)}(\omega_2)$ is determined according to the formula [2]

$$\Delta K_l^{(1)}(\omega_2) = N_l^{(0)}(\sigma''_{lc} - \sigma''_{vl}) \left[\frac{\sigma'_{vl}}{\sigma'_{lc} + \sigma'_{vl}} - \rho_l^{(0)}\right] \times$$

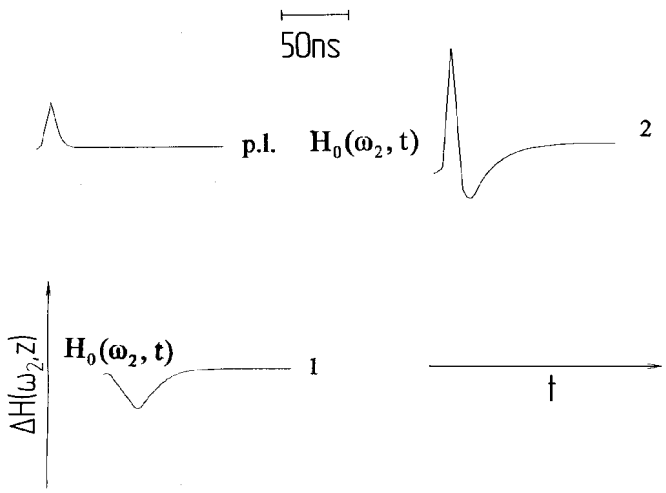

Fig. 1. Kinetics $\Delta H(\omega_2, t)$ at the point $\hbar\omega_2 = 1.56$ eV and $I_1 = 4$ MW/cm^2 in the 0.5% (*1*) and 1% (*2*) Bi-doped β-CdP_2 specimens. The laser pulse (p.l.) is depicted on the top

$$\times \left\{ 1 - \exp\left(-\frac{\sigma_{lc} + \sigma'_{vl}}{\hbar\omega_1} \int_0^t I(\omega_1, t)\, dt \right) \right\}. \qquad (2)$$

Here, $N_l^{(0)}$ is the concentration of l-centers, $\sigma'_{\nu l}$, σ'_{lc} and $\sigma''_{\nu l}$, σ''_{lc} are the cross-sections of the quantum absorption of the laser ($'$) and sensing ($''$) light beams for the induced transitions of electrons and holes between the impurity centers l and the energy bands v and c, t is time, $\rho_l^{(0)}$ is the electron population of the l-centers at the laser ignition time ($t = 0$), and $I(\omega_1, t)$ is the intensity of the laser beam. The spectrum $\Delta K_l^{(1)}(\omega_2)$ is determined by the spectral dependences of the absorption cross-sections $\sigma''_{\nu l}$ and σ''_{lc}. The values of $\sigma''_{\nu l}$ and σ''_{lc}, their frequency dependences and maximum positions are essentially defined by the depth of the impurity level and on the impurity charge state after either its ionization or deionization. But in every case of the induced optical transitions of electrons and holes between the deep impurity M_0-centers and the energy bands, the spectral bands will be obtained in the form of the steps up- or downwards into the short-wave range, or, for the M_3-points, into the long-wave one. Sharp cusps in the neighborhood of those points correspond to the distances of the singularity points in the electron density of states reckoned from the deep impurity energy level l in the gap. Moreover, the points of the spectra $\sigma''_{\nu l}$ and σ''_{lc} with the energy of the quanta $\hbar\omega_2 = |E_{M_0} - E_l|$ are the beginning of the steps into the short-wave region, and, with the energy $\hbar\omega_2 = |E_{M_3} - E_l|$, are the beginning of the steps into the long-wave one. Here, E_{M_3} and E_{M_0} are the electron and hole energies in Van Hove singularities of the M_3 and M_0 types, respectively, E_l is their energy at the l-centers. The general structure of $\Delta K_l^{(1)}(\omega_2)$ is expressed by a factor $\pm(\sigma''_{lc} - \sigma''_{\nu l})$, where the sign plus corresponds to the case $\rho_l^{(0)} > \frac{\sigma'_{vl}}{\sigma'_{lc}+\sigma'_{vl}}$, and the sign minus to the inverse one, $\rho_l^{(0)} < \frac{\sigma'_{vl}}{\sigma'_{lc}+\sigma'_{vl}}$. That is, if $\sigma'_{\nu l} = 0$ and $\sigma'_{lc} \neq 0$, then the transitions between the M_0-points in the valence band and the l-centers will be described in the spectrum $\Delta K_l^{(1)}(\omega_2)$ by a step upwards into the short-wave region, while the transitions between the l-centers and the M_0-points in the conduction band by a step downwards into the same region. The transitions between the M_3-points in the valence band and the l-centers are marked by a step upwards into the long-wave region, and the transitions between the l-centers and the M_3-points in the conduction band by a step downwards also into the long-wave region. Those features make it possible, on the basis of the experimental spectra $\Delta K_l^{(1)}(\omega_2)$, to determine the availability and the depth of the impurity l-levels, provided that the depth of the M_0- and M_3-point positions in the bands are known, and, vice versa, one can evaluate the depth position of the M_0 and M_3 critical points, provided that the depth of the l-level is known.

The absorption coefficient $\Delta K(\omega_2, t)$ was calculated in accordance with the formula [1]

$$\Delta K(\omega_2, t) = \frac{1}{d} \ln \frac{1}{1 - \frac{\Delta H(\omega_2, t)}{H_0(\omega_2)}}, \qquad (3)$$

where $\Delta H(\omega_2, t)$ is the kinetics obtained during the action of the pump wave $\hbar\omega_1$ on the crystal, $H_0(\omega_2)$ is a deviation from the zero level due to the action of the sensing wave $\hbar\omega_2$, and d is the specimen width.

2. Results and Discussion

In Fig. 1, the kinetics $\Delta H(\omega_2, t)$ is presented. It is seen that the form of the curve for the undoped crystals is similar to that of the pulse of the laser (*p.l.*).

In Fig. 2, the spectra $\Delta K(\omega_2)$ are shown for the laser pulse duration $t = 15$ and 35 ns. Each point is a result of averaging over many tens of measurements. Here, $\mathbf{q}_1 \parallel \mathbf{q}_2 \parallel \mathbf{c} \perp \mathbf{e}_1 \parallel \mathbf{e}_2$, where $\mathbf{q}_1$ is the wave vector of the laser beam, $\mathbf{q}_2$ is the wave vector of the sensing wave, both having the same direction, $\mathbf{c}$ is the optic axis of the crystals, and $\mathbf{e}_1$ and $\mathbf{e}_2$ are the polarization vectors of the pump and sensing waves, respectively.

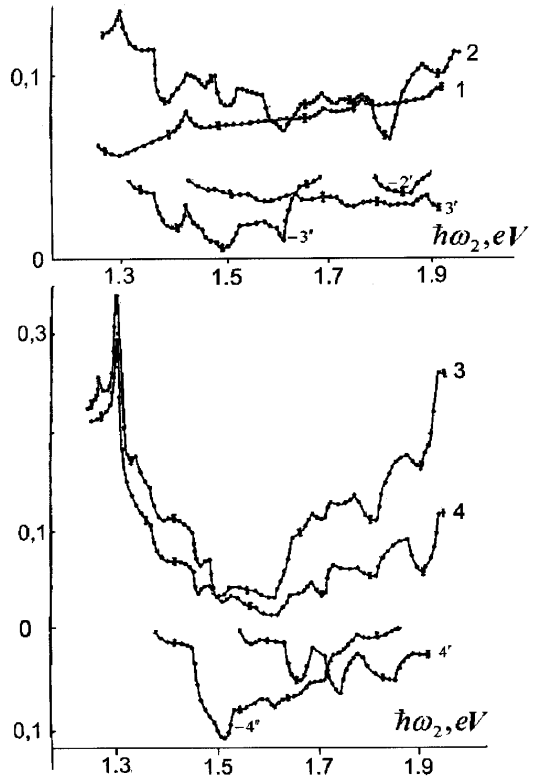

Fig. 2. Spectra $\Delta K(\omega_2, t)$ of the undoped (*1*), 0.5% (*2* and *2'*), and 1% (*3*, *3'*, *3''*, *4*, *4'*, and *4''*) Bi-doped specimens. Spectrum *1* corresponds to the maximal kinetics value, spectra *2*, *3*, and *4* were measured at $t = 35$ ns; *2'*, *3'*, and *4'* at $t = 200$ ns; *3''* and *4''* at $t = 10 \div 15$ ns. Spectra *1*, *2*, *2'*, *3*, *3'*, and *3''* are obtained at $\mathbf{q}_1 \parallel \mathbf{q}_2 \perp \mathbf{c} \parallel \mathbf{e}_1 \parallel \mathbf{e}_2$; spectra *4*, *4'*, and *4''* at $\mathbf{q}_1 \parallel \mathbf{q}_2 \perp \mathbf{c} \perp \mathbf{e}_2$ and the circular polarization of the laser beam

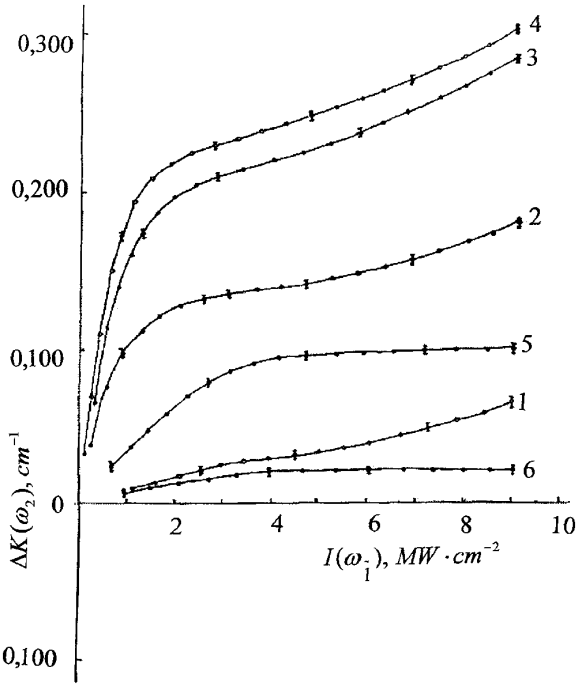

Fig. 3. Dependence of $\Delta K(\omega_2, t)$ on the intensity I_1 at $\hbar\omega_2 = 1.28$ eV for the undoped (*1*), 0.5% (*2*) and 1% (*3* and *4*) Bi-doped specimens. Dependences *1* to *3* were obtained at $\mathbf{q}_1 \parallel \mathbf{q}_2 \perp \mathbf{c} \parallel \mathbf{e}_1 \parallel \mathbf{e}_2$, and dependence *4* at $\mathbf{q}_1 \parallel \mathbf{q}_2 \perp \mathbf{c} \perp \mathbf{e}_1 \perp \mathbf{e}_2$. Dependences *5* and *6* correspond to the heights of the bands $\hbar\omega_2 = 1.30$ and 1.27 eV, respectively, in spectrum *4* in Fig. 2

In the spectra of undoped crystals (*1*), the bands with maxima at $\hbar\omega_2 = 1.43$, 1.69, and 1.77 eV manifest themselves. The latter two bands were investigated in [3]. The conclusion was made that those bands correspond to the electron transitions in donor-acceptor pairs composed of deep acceptors (the double-charged Cd vacancies) and shallow donors (the substitutional atoms, *S*), which occupy the phosphorus sites in the second and first coordination spheres relatively to the Cd-vacancies. The band of 1.43 eV corresponds to the resonance two-photon absorption [4].

In Fig. 3, the intensity dependences $\Delta K(\omega_2, t)$ are depicted. Curve *1* corresponds to $t = 15$ ns, curves *2*–*4* to $t = 35$ ns.

The kinetics of the photocurrent $\Delta I(t)$ are shown in Fig. 4,*a* for the undoped specimen (*1*) and for two specimens, Bi-doped to 0.5% (*2*) and 1% (*3*), at $I_1 = 4$ MW/cm^2. The dependences of the maximal values of the photocurrent kinetics on the intensity of the laser pulses I_1 are displayed in Fig. 4,*b*. While comparing the intensity dependences $\Delta K(\omega_2)$ measured at $\hbar\omega_2 = 1.30$ eV (see Fig. 3) with the dependences $\Delta I(t)$ in Fig. 4,*b*, one can see that the spectra of the doped specimens are much more involved than those of the undoped crystals.

The peculiarities of the spectra (see Fig. 2) of 1% Bi-doped specimens are narrow bands with maxima at $\hbar\omega_2 = 1.27$, 1.30, 1.35, 1.43, 1.69, and 1.77 eV and steps at $\hbar\omega_2 = 1.30$, 1.31, 1.37, 1.40, 1.46, 1.47, 1.49, 1.53, 1.55, 1.58, 1.61, 1.62, 1.64, 1.65, 1.70, 1.72, 1.73, 1.75, 1.78, 1.79, 1.82, 1.88, 1.91, and 1.94 eV. While comparing the spectrum structure of the 0.5% Bi-doped specimen (*2*) with those of the 1% Bi-doped ones (*3*, *3'*, and *3''*), an essential distinction is seen, but all singularities of spectrum *2* are also inherent in curves *3*, *3'*, and *3''*. Spectrum *2* also manifests well singularities which correspond to the discovered in [3] impurity levels d_1, d_2, and d_3, situated in the energy gap at the distances of 0.43, 0.61, and 0.85 eV, respectively, from the bottom

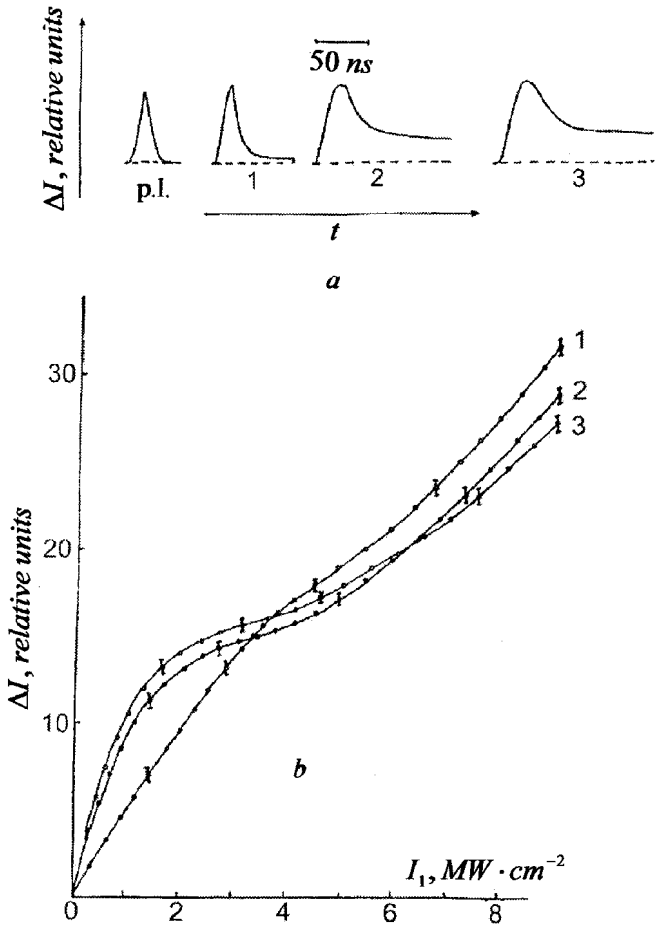

Fig. 4. Kinetics of the photocurrent $\Delta I(t)$ at $I_1 = 4$ MW/cm^2 (*a*) and the dependences of the maximal values of the photocurrent kinetics on the laser pulse intensity I_1 (*b*) for undoped (*1*), 0.5% (*2*) and 1% (*3*) Bi-doped specimens

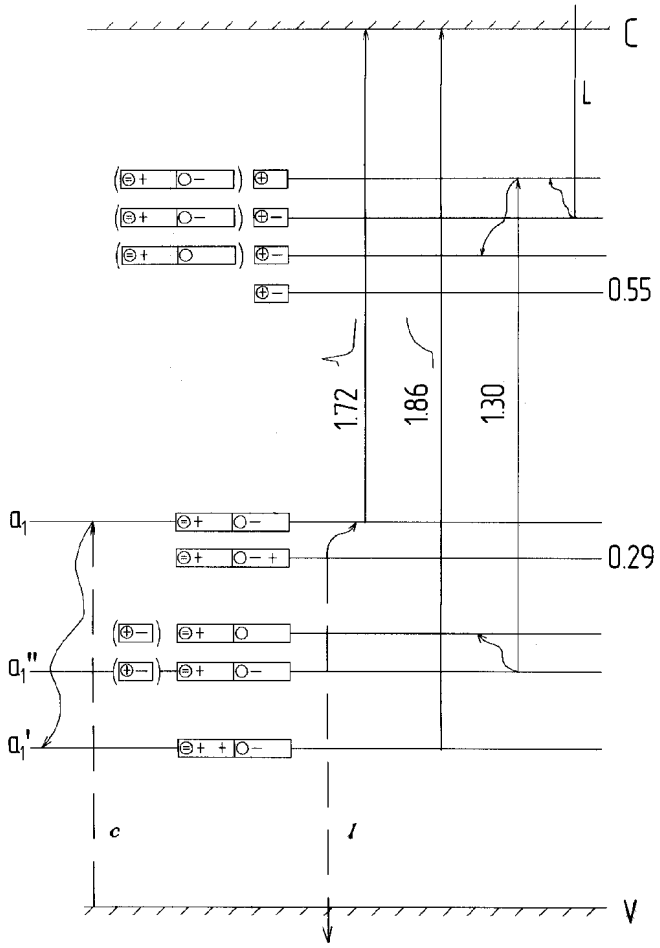

Fig. 5. Structure scheme of the impurity complexes and relevant electron transitions in β-CdP_2:Bi

of the conduction band, as well as the impurity level d in the energy gap near the bottom of the conduction band, which has not been discovered in [3]. In spectra *2′* and *4′*, the band with a long-wave edge at about 1.79 eV, which was not identified in [3], is also seen. This band is similar to the band clearly manifested in spectrum *4′* with long-wave edges at 1.55, 1.64, and 1.70 eV. The band with a long-wave edge at 1.86 eV is well distinguishable in the spectrum of the slow component *2′* as well as in spectra *3′* and *4′*. Moreover, the presence of the fast positive term and very slow negative one in the kinetics $\Delta K_l^{(1)}$ (ω_2) of the band of 1.72 eV, and of the similar slow but positive term in the kinetics of the band of 1.86 eV, evidences for the interconnection between the levels a_1 and a_1'. It can be explained in such a way that those levels belong to the same triple-charged centers, which may be the complexes composed of their own defects (they are the double-charged Cd vacancies) and of the isoelectron spontaneous impurities of Zn, whose atoms substitute for Cd at the crystal lattice sites. In this case, there will be a system of electron transitions shown in Fig. 5. The circles with double minus represent the non-compensated local charges caused by the absence of Cd atoms at the crystal lattice sites, the dotted circles correspond to the neutral isoelectron centers, the circles with plus to non-compensated local charges of the centers Bi_{Cd}, the plus designates a hole, and the minus designates an electron. Curve V corresponds to the top of the valence band, and curve C to the bottom of the conduction one. The vertical straight lines are used to designate the optical transitions of electrons being subjected to the laser (L) and testing (1.30, 1.72, 1.86) beams. The wavy arrows correspond to the transition of the impurity centers, stimulated by the phonon exchange, into new energetic states after

their ionization or deionization. Dashed lines are used for spontaneous (c) and non-forbidden stimulated (l) transitions between the centers and the valence band. The kinetics $\Delta K_l^{(1)}(\omega_2)$, which correspond to the bands with long-wave edges of 1.72 and 1.86 eV, are also shown. For the band of 1.72 eV, such kinetics are composed of the short initial positive region and the succeeding long negative one. The maximal values of those long-term components are at about the period of 500—550 ns. This means that the long-term regions of the kinetics of the bands of 1.72 and 1.86 eV correspond to the electron concentration variation at the local centers a_1 and a_2' due to the recombination processes [3]. Those processes must be very intense and can occur in the complexes depicted in Fig. 5. The behavior of the long-term kinetics of the bands of 1.72 and 1.86 eV may be stipulated by a spontaneous trapping of unbalanced holes from the valence band by the complexes in the a_1 state. The large concentration of the unbalanced holes, generated by the laser pulse, is a result of two-photon absorption and because the process of the spontaneous trapping of the unbalanced holes by the complexes in the a_1' state is impossible. In spectrum *2* (Fig. 2), the band with a long-band edge of 1.72 eV reveals itself to a less extent than in spectra *3* and *3′*. According to the diagram displayed in Fig. 5, this is explained by the fact that the conductivity of the n-type manifests itself more poorly in the specimens with lower doping level (0.5% Bi) than in the higher-doped ones (1% Bi). So, the number of the complexes in the state a_1 in the specimens with a lower doping degree is smaller than in the case of a specimen with a higher doping level.

In contrast to the 1% Bi-doped specimens, in the spectra of which there are powerful bands with the maxima at 1.27 and 1.30 eV, those bands are essentially weaker in the spectra of the 0.5% Bi-doped specimens. They are absent altogether from the spectra of Zn- and Se-doped specimens. So, it is naturally to suggest that those bands are governed by the impurity centers, in the generation of which the Bi impurities take part.

The bands of 1.27 and 1.30 eV can be stimulated by both the intra-center and inter-impurity transitions in the system "neutral center or complex – charged center". Fig. 3 shows the dependences of the heights of those bands in spectrum *4* (Fig. 2) on the intensity of the laser pulse (curves *5* and *6*). Their heights were estimated as the distance between the peak summit of the spectral band and the interpolation line, which separated the spectral band from its pedestal. We see that the intensity dependences of the bands of 1.27 and 1.30 eV are similar to each other. It is of great importance that a Bi impurity is of the isoelectron type in respect to P. To create a local level by an isoelectron atom, a rather large difference between the isoelectron substitutional atom and that of the main crystal lattice is required. The more the difference, the deeper should be the local level relatively to the edge of the energy gap. The Bi atom has an essentially greater atomic number than the P atom. In this case, the short-range forces attract the hole, and an isoelectron donor appears. After the hole has been trapped, an electron is attracted by Coulomb forces to the created charged donor. Such donors will create shallow levels in the energy gap. But due to the great discrepancy between the tetrahedral radii of Bi and P atoms and to the proximity of the relevant values for Bi and Cd atoms, the substitution of Cd atoms by Bi ones should be more profitable. The decrease of the specific conductance is provided by impurities, which can occupy Cd vacancies or substitute Cd atoms in the lattice [5]. Those centers will be donors. Due to such properties of Bi atoms, the intense substitution of Cd and P atoms by Bi ones may take place in the process of doping. In the first case, the levels d will be created in the energy gap at a depth of 0.55 eV from the bottom of the conduction band; in the second case, the shallow donor levels are created. The energy levels d_4, which are connected to the bands with the long-wave edges of 1.30 and 1.91 eV, are depicted in Fig. 6. Those levels can belong to the Bi atoms that occupy the P sites in the lattice. The energy levels d_2 can belong to the P vacancies. They are clearly seen in spectrum *2*, in contrast to the undoped specimens, which possess the conductivity of the p-type. As the doping level increases up to the 1% Bi-concentration, the concentrations of the d- and d_4-centers also increase. Some of the d-centers are created near the Zn atoms, which substitute the Cd ones and make up bonds between impurities. The sufficient concentration of the pairs $\mathrm{Bi_{Cd}}$–$\mathrm{Zn_{Cd}}$ is attained, where the impurity–impurity transitions of electrons manifest themselves as the appearance of an intense narrow band with the maximum at $\hbar\omega_2 = 1.30$ eV (see Figs. 2 and 6). The conclusion that the d_2 level belongs to P vacancies agrees with the experimental results of [6].

If the ground state energy of an electron on a donor, reckoned from E_c, equals E_D, the ground state energy of a hole on an acceptor, reckoned from E_v, equals E_A, and their Coulomb interaction is determined by the static dielectric permittivity ε, then the energy of an absorbed quantum at the electron transition is

$$\hbar\omega_2 = E_g - (E_D + \Delta E_D + E_A) + \frac{q^2}{\varepsilon R} + \Delta E. \qquad (4)$$

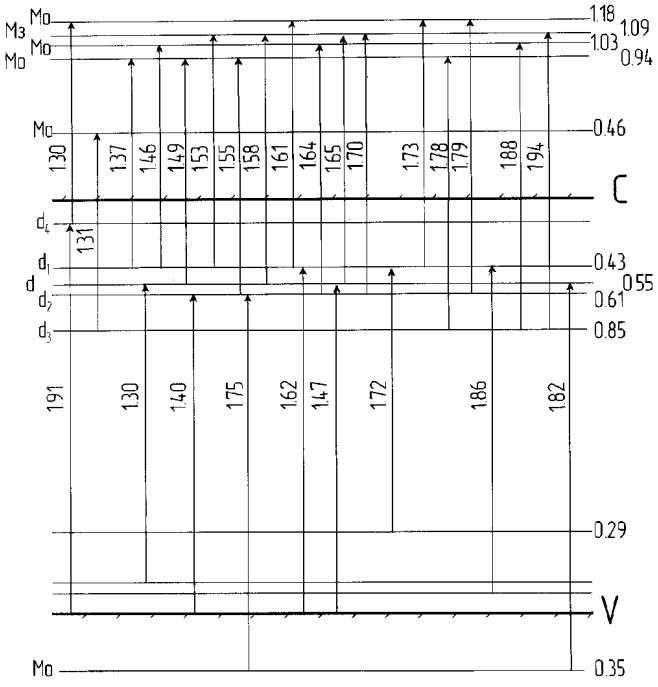

Fig. 6. Scheme of the impurity energy levels, singularities of the first kind in the v- and c-bands, and optic transitions of electrons in β-CdP_2:Bi

The value of ΔE tends to zero for far pairs and is finite for near ones. It is determined by the overlapping of the ground state wave-functions of the donor and acceptor and characterizes a distinction of the interaction from the simple Coulomb one. ΔE_D is a correction to the electron energy on the donor, which is stipulated by the shift in accordance with the Franck-Condon principle.

If neutral centers participate in the impurity-impurity absorption, the Coulomb interaction has to be absent, the energy values for the transitions of electrons in pairs with different R's should be unlike only due to the overlapping of wave-functions, and the spectral line positions for the interimpurity transitions will be practically independent of R. In our case, the neutral center is an isoelectron Zn impurity.

Taking into account the same dependence of the bands of 1.30 and 1.27 eV on the intensity, the band of 1.27 eV may be identified as a phonon duplication of the band of 1.30 eV. The energy of the absorbed phonon is of about 30 meV. The band of 1.27 eV appears in the case $\mathbf{e}_2 \perp \mathbf{c}$, while in the case $\mathbf{e}_2 \parallel \mathbf{c}$, it becomes unnoticed. In [7], phonons with a polarization $\mathbf{e}_2 \perp \mathbf{c}$ and an energy of 31.7 meV were discovered in CdP_2, in the spectra modulated by the wavelength of absorption. Phonons with a similar energy value of (30.3±0.3) meV also intensively manifested themselves in the Raman spectra of CdP_2 for the light with a polarization $\mathbf{e} \perp \mathbf{c}$ [8].

Conclusions

The absorption spectra obtained during the study of the Bi-doped crystals are much more involved than those measured for the undoped specimens of β-CdP_2. After the detailed analysis of the obtained experimental results, the schemes of the impurity complex structure (Fig. 5), the impurity energy levels, and singularities of the first kind in the v and c bands (Fig. 6), as well as those of the corresponding electron transitions, have been built. They explain the features of the kinetics' structure, spectra, and intensity dependence $\Delta K_l^{(1)}(\omega_2)$ for Bi-doped β-CdP_2 crystals. A spectral band with the maximum at $\hbar\omega_2 = 1.30$ eV, which probably belongs to the impurity-impurity transitions, and a band of 1.27 eV, which corresponds to the phonon absorption with an energy of 30 meV, have been discovered.

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АНАЛІЗ СПЕКТРІВ ПОГЛИНАННЯ КРИСТАЛІВ β-CdP_2, ЛЕГОВАНИХ Bi

І.І. Пацкун, І.А. Слипухіна

Р е з ю м е

Наведено результати спектральних і інтенсивнісних досліджень нелінійного поглинання у кристалах β-CdP_2, легованих Bi. На основі теоретичного аналізу побудовано схеми домішкових енергетичних рівнів у v- і c-зонах і оптичних переходів електронів в β-CdP_2:Bi, а також запропоновано схему структури домішкових комплексів.