Optical and photoelectric properties of vanadium-doped Cd$_{1-x}$Hg$_x$Te crystals

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Abstract
Vanadium-doped semi-insulating $Cd_{1-x}Hg_x$Te ($x < 0.05$) n-type crystals were grown by the Bridgman technique for the first time. Studies were carried out of the low-temperature optical and photoelectric properties of $Cd_{1-x}Hg_x$Te ($x = 0.014$), which provided information on the deep anisotropic impurity centres and intrinsic defects. The nature and the position of their energy levels with respect to the crystal energy band were determined. It was shown that for the investigated crystals there are two photogeneration mechanisms of electrons from deep impurity levels: the auto-ionization of electrons from the discrete state, which is in resonance with the conduction band, and their direct photoionization. It was found that the photosensitivity region for $Cd_{0.986}Hg_{0.014}$Te:V crystals is about 1.3 μm.

1. Introduction

At present there is a strong need for sensitive fast nonlinear optical devices with potential applications in the areas of optical communications, optical storage, optical computing and optoelectronics [1]. In the past most of the fundamental and applied studies of photorefractive materials have been concentrated on ferroelectric oxides, but in recent years increased attention has been given to semiconductors because of their significantly lower response time and high sensitivity in the near-IR region. Among the semiconductor materials currently studied for their photorefractive properties CdTe was very promising for applications in the near-IR region. Bylsma *et al* [2] for the first time reported the observation of the photorefractive effect in vanadium-doped CdTe crystals at 1.06 μm. Other photorefractive studies [3, 4] as well as investigations of EPR, photo-EPR and optical spectra [5–9] of CdTe:V crystals were carried out. The modern state of investigations of photorefractive semiconductor materials shows that

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it is important to carry out detailed studies of their different physical properties. It should be noted that even in the most studied case, CdTe:V, the impurity incorporation mechanisms require further studies. The status of controlling intrinsic defects in CdTe:V and the formation of complex impurity centres are the first stage of understanding.

It should be pointed out that the photosensitivity of CdTe:V in the long-wave region is about 1.0 μm [10]. On the other hand it was known [1] that the 1.3–1.5 μm spectral region is technologically important for optical telecommunication using low-powered semiconductor lasers ($\sim$1 mW). Therefore the elaboration of new photorefractive semiconductor materials for this region is an urgent scientific and technological problem. It should be also noted that the impurity states of V atoms in CdTe play a decisive role in the appearance of its photorefractive properties. Photoionization of these impurity centres (V^{2+}) results in the formation of free carriers. At the same time, ionized deep impurity centres (V^{3+}) may function as traps for photoexcited carriers. Therefore, the acquisition of the most comprehensive information concerning the energy and crystal structure of deep-impurity centres is very important so as to determine the micromechanism of the photorefractive recording of information in these crystals.

The main task of the present work is the growth of semi-insulating $Cd_{1-x}Hg_xTe$ ternary alloys doped with vanadium atoms and the characterization of their intrinsic defects and impurity centres. Since the bandgap of these crystals is reduced as compared with CdTe, they allow us to tune the photoionization energy of dopants and to extend the photosensitivity range of these materials. It should be noted that the insertion of Hg atoms of rather small concentration (a few per cent) allows us to obtain $Cd_{1-x}Hg_xTe$:V crystals, which will have photosensitivity at 1.5 μm. Therefore, these crystals may be considered as new promising photorefractive materials. It is also important to note that the insertion of Hg atoms in CdTe increases the electro-optic coefficient and thus improves its potential photorefractive properties.

In this paper low-temperature studies of the optical and photoelectric properties of $Cd_{1-x}Hg_xTe$ ($x = 0.014$) crystal doped with vanadium are carried out in order to detect intrinsic structural defects and anisotropic impurity complexes, to establish their nature and the position of the energy levels and also to determine the photosensitivity region of these crystals.

2. Experimental procedures

The vanadium-doped $Cd_{1-x}Hg_xTe$ ($x \leqslant 0.05$) semi-insulating crystals were grown by the vertical Bridgman technique for the first time. Doping was achieved by incorporation of vanadium into the melt. Initial concentration of the dopant impurities was about 10^{19} cm^{-3}. The elements were carefully weighed to obtain the desired molar composition and impurity concentration. The Hg atom concentration was also determined taking into account the energy position of the exciton reflection band [11]. Prior to the synthesis of the $Cd_{1-x}Hg_xTe$:V alloys, single elements Cd and Te were purified by vacuum sublimation. The crystal ingots of 80 mm length and diameter 14 mm were obtained. Single crystals of dimensions $8 \times 8 \times 5$ mm^3 were cut from different parts of the ingots. All samples obtained had n-type conductivity with resistance of 10^6–10^8 Ω cm. The samples were oriented by a DRON-3 x-ray diffractometer.

The absorption and photogalvanic-current (PGC) spectra were measured with a KSVU-23 device. The input resistance of the electrometer was much lower than the resistance of the samples, so in these experiments we measured a diffusion current close to the short-circuit current. The polarity of the photogalvanic (photodiffusion) current was determined by the polarity of the charge observed at the front (illuminated) surface of the sample and was opposite to that of the excited carriers [12].
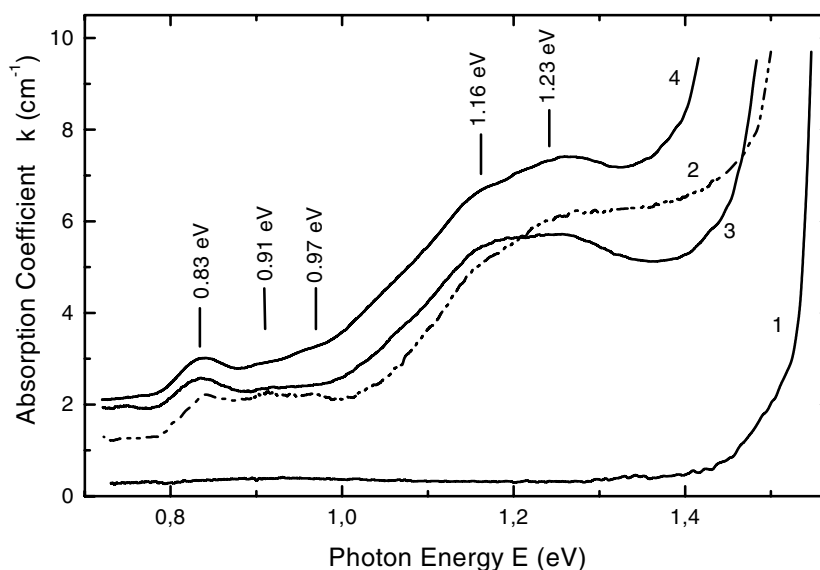
Figure 1. Absorption spectra of CdTe (curve 1), CdTe:V (curve 2) and $Cd_{1-x}Hg_xTe$ crystals ($x = 0.014$ and 0.037, curves 3 and 4, respectively), $N_V = 10^{19}$ cm^{-3} at 78 K.

3. Experimental results and discussion

The absorption spectra of CdTe and $Cd_{1-x}Hg_xTe$ crystals doped with vanadium atoms as well as pure CdTe are shown in figure 1 at 78 K. One can see from the curves displayed in figure 1 that a long-wavelength shift of the absorption edge is observed with growth of Hg atom concentration due to the decrease of the bandgap of the crystals [11]. The position of the absorption bands corresponds to the intracentre absorption of the V impurity ions of different charge states as well as photoionizing absorption spectra. According to [13, 14], the absorption band in the long-wave region near 0.8 eV corresponds to the intracentre absorption between $^4T_1(F)$ and $^4A_2(F)$ states of the V^{2+} impurity ions. For CdTe:V, $N_V = 10^{19}$ cm^{-3} (curve 2) as compared with $Cd_{1-x}Hg_xTe$ ($x = 0.014$ and 0.037, curves 3 and 4, respectively), the additional absorption bands at 0.91 and 0.97 eV, which indicate the existence of V^{2+} and V^{3+} centres in CdTe:V crystals, were revealed [3]. The wide absorption band near 1.20 eV is due to both the intracentre transitions between the $^4T_1(F)$ and $^4T_1(P)$ states of the V^{2+} impurity ions and their overlap with the photoionization absorption.

As shown in figure 1, the increase of Hg atom concentration in the $Cd_{1-x}Hg_xTe$ crystals leads to the increase of the background absorption, which is mainly caused by the light scattering by crystal inhomogeneity formed as a result of the nonuniform distribution of both composition components and V impurity centres. It should be noted that the solubility of vanadium in CdTe is close to that of $Cd_{0.986}Hg_{0.014}Te$ crystals since the absorption coefficients of intracentre transitions of V^{2+} ions for these crystals (figure 1, curves 2 and 3, respectively) are approximately equal.

It is known [12] that exciton excitations are highly sensitive to various types of defect and impurity in the crystal. Therefore we also performed studies of the exciton reflection and photoluminescence spectra for the $Cd_{0.986}Hg_{0.014}Te:V$ crystal at 78 K. The broadening of the exciton reflection band compared with the CdTe:V crystal was observed (about three times). It should be noted that the photoluminescence line corresponds to the emission of excitons bound
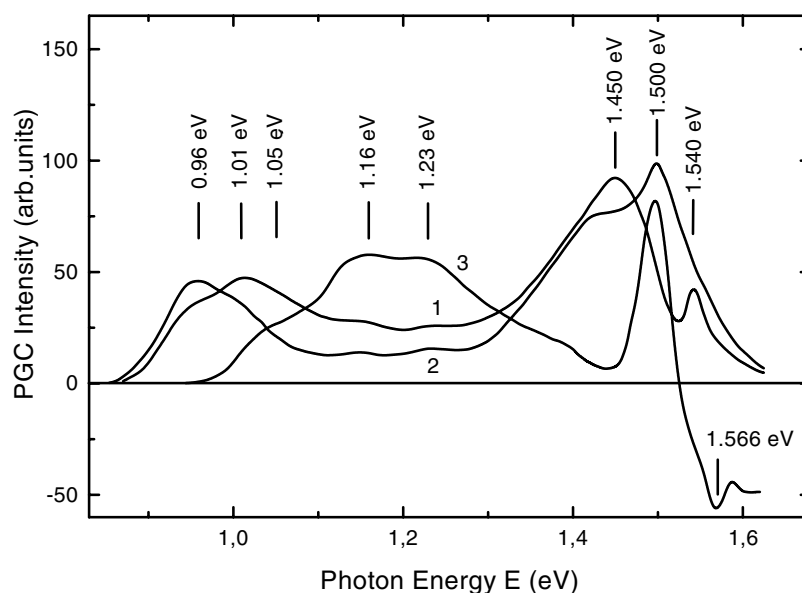
Figure 2. PGC spectra of the $Cd_{0.986}Hg_{0.014}Te:V$ crystal (curves 1 and 2, the propagation of light in the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions, respectively) and CdTe:V (curve 3, $\langle 111 \rangle$ direction), $N_V = 10^{19}$ cm^{-3} at 78 K.

on the acceptor centres (A^0 X line). By analogy to the exciton reflection band the A^0 X line is also broadened. The fact that low-temperature exciton reflection and photoluminescence spectra are observed indicates that the investigated crystal is of fairly good crystalline quality. The energy position of exciton reflection band is practically the same as for the opposite sample surface. This indicates that this sample had a very satisfactory homogeneity.

Information on the energy position of the levels of deep impurity centres and intrinsic defects relative to the crystal energy bands may be obtained by measuring the PGC spectra [12, 15]. In the PGC spectra of these crystals (figure 2) the positive bands are caused by photoionization transitions of electrons from impurity or defect levels to the conduction band, while the negative bands are attributed to the excitation of valence-band electrons to discrete levels positioned in the crystal bandgap [12]. In figure 2 there are the PGC spectra which correspond to the propagation of light in the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions of $Cd_{1-x}Hg_xTe$ crystals (curves 1, 2, respectively) as well as the PGC spectrum of the CdTe:V crystal for the $\langle 111 \rangle$ direction (figure 2, curve 3). The arising of the most intense band near 1.500 eV is caused by the presence of intrinsic defects of acceptor type in the investigated crystals. Such acceptors are the singly charged centres consisting of doubly charged cadmium vacancy (V_{Cd}^{2-}) and a singly ionized donor (D_+), i.e. the ($V_{Cd}^{2-} + D^+$)$^-$ centre [12]. The nature of the donor atom determines the energy of these acceptors, that is in the range $E_v + (0.10–0.15)$ eV [12, 16, 17]. The high-energy positive band at 1.590 eV is caused by exciton dissociation. The negative band at 1.566 eV is probably caused by the transition from the valence band to the donor level at E_c—0.035 eV, formed by the singly ionized donor (vacancy of Te atom) [18].

The PGC spectrum of the CdTe:V crystals also exhibits a broad structured band in the long-wavelength spectral range. The long-wavelength wing of the PGC band reveals a kink near 1.05 eV which is due to the direct photoionization energy of V^{2+} centres. This energy is close to the value ($\sim$1.0 eV) obtained by photoconductivity measurements [10]. The observed

maxima of the PGC bands at 1.16 and 1.23 eV coincide with the energy positions of the broad absorption band in CdTe:V (figure 1, curve 2). This suggests that the PGC bands are caused by the excitation of V^{2+} ions into the $^4T_1(P)$ state, which is in resonance with the conduction band. As a result of interaction of the discrete impurity state with the conduction band continuum, the auto-ionization of electrons from the excited impurity level to the conduction band occurs. It should be noted that the intensity of PGC bands caused by auto-ionization of electrons is considerably larger than that in the case of direct photoionization of electrons.

In figure 2 there are also shown the PGC spectra for the $Cd_{1-x}Hg_xTe$ crystals. In the long-wavelength region of the PGC spectra the intense positive bands at 1.01 and 0.96 eV are revealed when light propagates along the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions (curves 1 and 2, respectively), which correspond to the direct photoionizing transition from the main V^{2+} state to the conduction band. For the $Cd_{0.986}Hg_{0.014}Te$:V crystals (figure 2, curves 1, 2), by analogy with the CdTe:V crystals, in the PGC spectrum two bands at 1.16 and 1.23 eV are observed. However their intensities are considerably smaller as compared with that for the 0.96 eV and 1.01 bands. Thus in the case of $Cd_{1-x}Hg_xTe$:V crystals the main photogeneration mechanism of electrons from deep-impurity centres to the conduction band is caused by the direct photoionization transitions. In the case of the $Cd_{0.986}Hg_{0.014}Te$:V crystal the photosensitivity maximum in the long-wave region is determined by the intense bands at 1.01 and 0.96 eV which are due to the direct electron photoionization from the main state of V^{2+} ions. The difference between the values of direct photoionization energy of the CdTe:V and $Cd_{0.986}Hg_{0.014}Te$:V crystals (1.05 and 1.01 eV, respectively), when light propagates in the $\langle 111 \rangle$ direction, is equal to 40 meV. This value is close to the difference of bandgap energy of these crystals (33 meV). Such a decrease of the photoionization energy of V^{2+} centres in $Cd_{0.986}Hg_{0.014}Te$:V crystal was expected, since the impurity level of the V^{2+} centres for a certain group of crystals (for example, II–VI semiconductors and their alloys) is fixed relative to the vacuum level [19].

The obtained results indicate that the efficiency of the auto-ionization of electrons from $^4T_1(P)$ excited states of V^{2+} ions to the conduction band depends on the position of the discrete impurity level relative to the bottom of the conduction band. It should be noted that for the $Cd_{0.986}Hg_{0.014}Te$:V crystals the photosensitivity region extends up to 1.3 μm, that is caused by both the decrease of the bandgap of these crystals and the change of the electron photogeneration mechanism from deep-impurity states to the conduction band.

Analysis of the shape, intensity and energy position of double-peaked bands near 1.00 eV indicates that they are probably caused by availability in the $Cd_{1-x}Hg_xTe$ crystals of the anisotropic V^{2+} centres of trigonal and orthorhombic symmetry. The group of trigonal centres oriented in the $\langle 111 \rangle$ direction and the other three equivalent directions are effectively excited when light propagates in these directions [20]. In this case the orthorhombic V^{2+} centres are also excited particularly. The axis of the orthorhombic centre is oriented in the six equivalent $\langle 110 \rangle$ directions. The appearance of the trigonal V^{2+} centres may be caused by formation of the complex impurity $(V_{Cd}^{2+} + X_{Te})$ centres, where X can be residual impurities of group VII atoms positioned at anionic sites. Other possible trigonal V^{2+} centres may be complexes $(V_{Cd}^{2+} + V_{Te})$. The formation of this centre will lead to the local lowering of its symmetry from cubic (T_d) to trigonal (C_{3v}) symmetry. In this case the main $^4T_1(P)$ state is split into the $^4A_2(F)$ and $^4E(F)$ components (the lower state is the $^4A_2(F)$ level). The appearance of orthorhombic V^{2+} centres of C_{2v} symmetry may be caused by the formation of the complex $(V_{Cd}^{2+} + Z_{Cd})$ centres, whose axis is orientated in one of the $\langle 110 \rangle$ directions. It should be noted that in an earlier study [21] of EPR spectra in the $Cd_{1-x}Zn_xTe$:V crystals a complex V^{2+} centre having orthorhombic symmetry was revealed. For these crystals Z is the Zn atoms positioned in the near-cationic sites in one of the equivalent $\langle 110 \rangle$ directions. For the $Cd_{1-x}Hg_xTe$:V crystals Z can be the Hg atoms. In the case of the orthorhombic $(V_{Cd}^{2+} + Hg_{Cd})$ complex centre the main
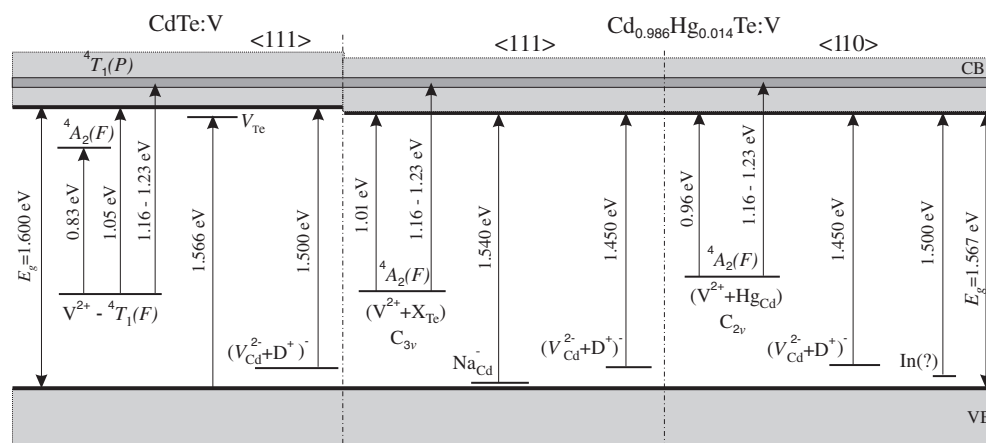
Figure 3. Combined energy-level diagram showing d–d* intracentre transitions and ionization levels of V impurity centres and intrinsic defects in CdTe:V and $Cd_{0.986}Hg_{0.014}$Te:V at 78 K.

$^4T_1(F)$ state is split by the C_{2v} symmetry crystal field into the three components ($^4A_2$, $^4B_1$ and $^4B_2$ states, where the orbital singlet $^4A_2$ is the lowest in energy).

It can be seen from figure 2 that in the short-wavelength region of PGC spectra (1.40–1.60 eV) there are observed broad bands. When light propagates in the $\langle 111 \rangle$ direction, the PGC spectrum of $Cd_{1-x}Hg_x$Te:V crystals consists of two positive bands near 1.450 and 1.540 eV. The high-energy band at 1.540 eV is probably caused by transition of electrons from the acceptor level $E_v + 0.028$ eV [18], which corresponds to a singly charged Na atom (residual impurity) positioned at a cationic site (Na_{Cd}^-) to the conduction band. The other band at 1.450 eV is caused by photoionization of a singly charged acceptor ($V_{Cd}^{2-} + D^+$)$^-$ complex. When light propagates in the $\langle 110 \rangle$ direction in the PGC spectrum (curve 2) the intense 1.500 eV band is observed, which may be caused by photoionizing transitions involving the acceptor level $E_v + 0.073$ eV, which was observed in the thermostimulation conductivity spectra of the CdTe crystals doped with In atoms [22].

In figure 3 the combined energy-level diagram showing d–d* intracentre transitions and ionization levels of V impurity centres and intrinsic defects in CdTe and $Cd_{0.986}Hg_{0.014}$Te is presented. The obtained results indicate that the main intrinsic defects in these crystals are the singly charged acceptor ($V_{Cd}^{2-} + D^+$)$^-$ complexes including the doubly charged cadmium vacancy (V_{Cd}^{2-}) and a singly ionized donor (D^+). For CdTe and $Cd_{1-x}Hg_x$Te crystals the ionization energies of such complexes are $E_v + 0.100$ and $E_v + 0.117$ eV, respectively. This may be caused by the participation of the different donor atoms. It can be seen from figure 3 that the $^4A_2(F)$ excited state of V^{2+} ions is in the bandgap of the crystal. The $^4T_1(P)$ excited state is in resonance with the conduction band. The auto-ionization energy of electrons from this excited state to the conduction band is 1.16–1.23 eV. In the case of the $Cd_{1-x}Hg_x$Te crystals the anisotropic V^{2+} centres of the trigonal (C_{3v}) and orthorhombic (C_{2v}) symmetry were determined. The direct photoionization energies of these centres are 1.01 and 0.96 eV, respectively.

4. Summary

In this study we have investigated vanadium-doped $Cd_{1-x}Hg_x$Te ($x = 0.014$) crystals by optical and photoelectric spectroscopies for the first time. All obtained samples had n-type

conductivity with resistance of 10^6–10^8 Ω cm. The optical absorption and PGC measurements provided information on the nature and the energy structure of anisotropic impurity centres and intrinsic defects. The combined energy-level diagram showing d–d* intracentre transitions and ionization level of V impurity centres and intrinsic defects is presented. These data are very important for the determination of the photorefractive effect mechanisms in these crystals. It was shown that the efficiency of the auto-ionization of electrons from the $^4T_1(P)$ excited state of V^{2+} ions which is in resonance with the conduction band depends on the position of the discrete impurity level relative to the bottom of the conduction band. For CdTe:V the auto-ionization electron mechanism is more effective and it determines the photosensitivity of the crystal in the long-wave region. In the case of $Cd_{1-x}Hg_xTe$:V ($x = 0.014$) the photosensitivity region is extended up to 1.3 μm, that is caused by the decrease of the energy gap and the change of the electron photogeneration mechanism (the direct photoionization is the main mechanism). It should be noted that a long-wave shift of the photosensitivity maximum for $Cd_{0.986}Hg_{0.014}Te$:V crystal as compared with CdTe:V is about 0.25 eV. In this case the decrease of the bandgap is only 0.04 eV. Analysis of the obtained results shows that under Hg concentration of about 7.5% it is possible to obtain semi-insulating crystals with the photosensitivity maximum in the near IR-region at 1.5 μm.

Acknowledgment

References

[1] Günter P and Huignard J (ed) 1989 *Photorefractive Materials and their Applications vols 1 and 2 (Springer Topics in Applied Physics vols 61 and 62)* (Berlin: Springer)
[2] Bylsma R B, Bridenbaugh P M, Olson D H and Glass A M 1987 *Appl. Phys. Lett.* **51** 889
[3] de Montmorillon L A *et al* 1996 *J. Opt. Soc. Am.* B **13** 2341
[4] Schwartz R N, Wang C-C, Trivedi S, Jagannathan G V, Davidson F, Boyd P R and Lee U 1997 *Phys. Rev.* B **55** 15 378
[5] von Bardeleben H J, Launay J C and Mazoyer V 1993 *Appl. Phys. Lett.* **63** 1140
[6] Schwartz R N, Ziari M and Trivedi S 1994 *Phys. Rev.* B **49** 5274
[7] von Bardeleben H J, Mazoyer V, Launay X and Launay J C 1995 *Semicond. Sci. Technol.* **10** 163
[8] Briat B, Ramaz F, Hamri A, Bardeleben H J, Launay J C and Mazoyer V 1995 *Semicond. Sci. Technol.* **10** 1629
[9] Christmann P, Meyer B K, Kreissl J, Schwarz R and Benz K W 1996 *Phys. Rev.* B **53** 3634
[10] Hoang L M and Baranowski J M 1977 *Phys. Status Solidi* b **84** 361
[11] Triboulet R 1977 *Rev. Phys. Appl.* **12** 123
[12] Gnatenko Yu P, Gamernyk R V, Faryna I A and Babij P I 1998 *Fiz. Tverd. Tela* **40** 1216 (Engl. transl. 1998 *Sov. Phys.–Solid State* **40** 1107)
[13] Slodowy P A and Baranowski J M 1972 *Phys. Status Solidi* b **49** 499
[14] Gnatenko Yu P, Gamernyk R V, Faryna I A, Blazhkiv V S and Krochuk A S 1996 *Fiz. Tekh. Poluprovodn.* **30** 1975 (Engl. transl. 1996 *Semiconductors* **30** 1027)
[15] Bukivskij P N, Gamernyk R V, Gnatenko Yu P, Pogorely V I and Faryna I O 1988 *Proc. 19th Int. Conf. on the Physics of Semiconductors (Warsaw 1988)* vol 2, ed W Zawadzki p 1103
[16] Slyn'ko V V, Babij P I, Gamernyk R V and Gnatenko Yu P 1994 *Fiz. Tekh. Poluprovodn.* **28** 506 (Engl. transl. 1994 *Semiconductors* **28** 310)
[17] Gamernyk R V, Gnatenko Yu P, Krochuk A S and Poslavskyj Z S 1988 *Ukr. Fiz. Zh.* **33** 1171
[18] Kröger F A 1977 *Rev. Phys. Appl.* **12** 205
[19] Zunger A 1985 *Annu. Rev. Mater. Sci.* **15** 411
[20] Kaplanskii A A 1964 *Opt. Spectrosc.* **16** 614
[21] Launay J C, Arnoux T and von Bardeleben H J 1997 *Semicond. Sci. Technol.* **12** 47
[22] Blasi C De, Micocci G and Tepore A 1977 *Rev. Phys. Appl.* **12** 255