Chapter 13
Photoluminescence of Nanocomposites Obtained by Heat Treatment of *GaS*, *GaSe*, *GaTe* and *InSe* Single Crystals in *Cd* and *Zn* Vapor

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Abstract The photoluminescence (PL) spectra of *GaS*, *GaSe*, *GaTe* and *InSe* semiconductors used as the basis materials to obtain nanocomposite by heat treatment in *Zn* and *Cd* vapor were studied. The PL spectra of *ZnS–GaS*, *CdSe–GaSe*, *CdSe–InSe*, *ZnSe–InSe* composites consist of wide bands covering a wide range of wavelengths in the antistokes region for *CdSe*, *ZnSe* and *GaS* crystallites from composites. The antistokes branches of spectra are interpreted as the shift of PL bands to high energies for nanosized crystallites.

13.1 Introduction

The material composed of semiconductor nanocrystallites of $A^{III}B^{VI}$ and $A^{II}B^{VI}$ type is obtained by heat treatment in the range temperatures of 623–1073 K of *GaS*, *GaSe*, *GaTe* and *InSe* single crystals in *Cd* and *Zn* vapor [1–3]. The *Ga*, *In*, *Zn* and *Cd* chalcogenides are luminescent materials in the wavelength range from UV to NIR. The photoluminescence spectrum of undoped *GaS* crystals at low temperatures ($T < 100$ K) contains a low intensity band localized in the region of indirect optical transitions. The structure of these bands is determined by the radiative

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annihilation of indirect exciton through phonons with the energy of 10 meV [4–6]. The intensity of impurity band with maximum at energy 1.24 eV prevails in the PL spectrum of *GaS* single crystals. The energy of the impurity PL band depends on the growth technology of the single crystal and the nature of structural defects and uncontrollable impurities. The *Mn*, *Zn* and *P* dopants form levels of self recombination in the bandgap that lead to the formation of intense PL bands with maximum at energies respectively of 2.00, 2.20 and 2.12 eV [6–8].

The PL spectra of *GaSe*, *GaTe* and *InSe* single crystals have a structure with one or two bands [9–12]. One of these bands corresponds to radiative annihilation of free or bound excitons with phonon repetitions and the other band is determined by the structural defects of crystal and impurities and the nature of uncontrollable dopants.

The copper as the dopant in concentrations from 0.1 to 1.0 mol% forms two donor levels with energies of $\sim$195 and 445 meV in the bandgap of the *GaSe* from the minimum of the conduction band in the center of Brillouin zone and four acceptor levels that energies are respectively 31, 51, 93 and 152 meV. The PL band is formed in the energy range of 1.6–2.0 eV with maximum at about 1.9 eV as the result of donor-acceptor recombination [13, 14]. The large PL bands are contained in the spectra of *GaSe* crystals doped with *Zn* [15].

The elements of group III (*Ga*) and VI (*Te*) form deep acceptor levels (175 meV) and donor levels with low energies respectively of 20 and 80 meV [16]. Acceptor levels that energy is in the range of 18–173 meV are formed in the bandgap of the *GaSe* compound by the elements from transition metal group like *Mn* and *Cr* [17–19].

The amount of *Cd* up to 1.0 mol% forms an impurity band with maximum at 1.21 eV with thermal activation energy of 0.17 eV in the PL spectrum of *InSe* crystals. The *Se* vacancies form a complex PL band with maximum at 1.31 eV. The intensity of this band depends on the granulation degree of *InSe* plate surface [19].

The $A^{II}B^{VI}$ semiconductors (*ZnS*, *ZnSe*, *CdS*, *CdSe*, *CdTe*) are luminescent materials in a wide range of wavelengths [20–22]. The PL and absorption bands of these materials as nanoparticles are shifted to higher energies when the size of crystallites decrease. It is experimentally established that the efficiency of PL increase when the size of these materials is reduced to nanometric dimensions. That's why these materials are widely used in the VIS region of the spectrum for PL devices [23].

The photoluminescence (PL) of nanocomposites obtained by heat treatment of *GaS*, *GaSe*, *GaTe* and *InSe* single crystals in *Zn* and *Cd* vapor is studied in this work.

13.2 Photoluminescence of Nanocomposites with *GaS* Lamellar Semiconductors

13.2.1 *Undoped* GaS *and* GaS *Doped with* Mn

The *GaS* is a lamellar semiconductor with indirect bandgap of 2.55 eV ($T = 293$ K) is considered a promising material for optoelectronic devices in visible and UV region of the spectrum [7, 24, 25]. The direct electronic transitions and indirect electronic

Fig. 13.1 The PL spectrum of *GaS* lamella at $T = 80$ K
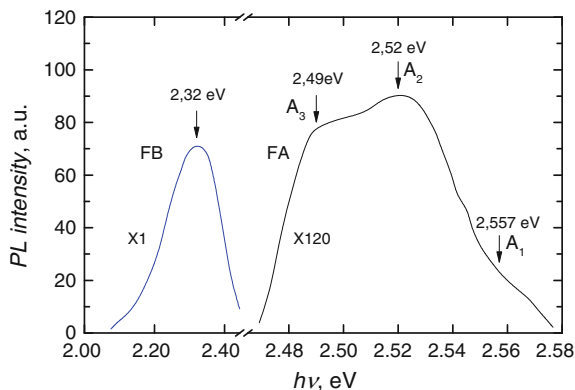
transitions (in the photoluminescence, photoconductibility and absorption spectra) at $T = 293$ K are allowed at energies higher than 3.0 eV. The photoluminescence (PL) spectrum of the *GaS* blades at $T = 80$ K consists of two bands A and B in the visible region (Fig. 13.1). It is known theat band A is formed by overlay of at least three bands with peaks at 2.557 eV (A_1), 2.520 eV (A_2) and 2.490 eV (A_3). The indirect free exciton emission band with maximum at energy of 2.571 eV is located near the fundamental absorption band edge [4, 26].

The process of luminescent emission at low temperatures as the result of indirect exciton annihilation is performed simultaneously with emission of phonons with the energy $\hbar\omega_f = 10$ meV [4]. The width of indirect bandgap at the temperature of 80 K for *GaS* crystals is equal to the sum of:

$$E_{gi} = E_{exi} + R_{ex} + \hbar\omega_f, \qquad (13.1)$$

where R_{ex}—is the energy of indirect free exciton binding.

It is obtained the value of $E_{gi} = 2.595$ eV for $E_{exi} = 2.571$ eV and $R_{ex} = 14$ meV. The band A_1 (Fig. 13.1) can be interpreted as luminescencent recombination of localized indirect exciton with the binding energy of 14 meV.

The bands A_2 and A_3 with broad contour prevail as intence in blue region of the spectrum and it can be associated with donor–acceptor type recombination. These bands are shifted to lower energies from the emission band of indirect free excitons with the energy of 71 and 64 meV. The energies of these bands do not depend on the dopant presence, such as *Mn* [6], *Zn* [27], *Cu* [5] and are shifted from the line of indirect excitons to highest energies than fundamental optical phonons energy in the *β–GaS* crystals whose energies are equal to 36.6 meV (transverse optical phonon) and 44 meV (longitudinal optical vibrational mode) [28]. It is known that longitudinal optical phonons may not participate in the luminescence generation–recombination processes.

The pronounced thermal attenuation of A_1 and A_2 bands whose intensities at 120 K are at the measurements background level serve as indicator of their excitonic nature. Since the free indirect exciton emission band is located at 2.571 eV
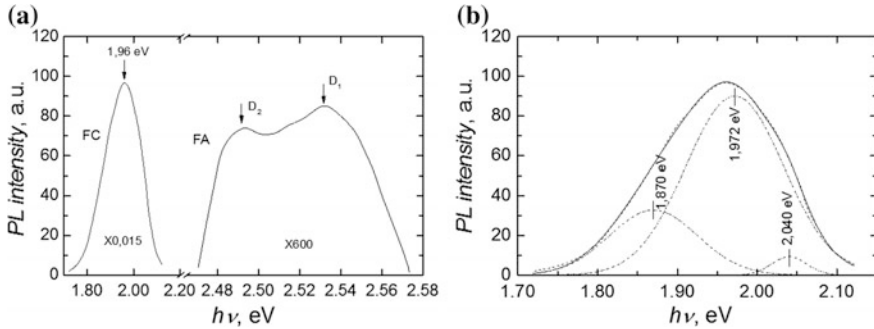
Fig. 13.2 The PL spectra at $T = 80$ K, of *GaS* lamella doped with 1.0 at.% *Mn* (**a**) and the deconvolution of C band in elementary bands (**b**)

and occurs with phonon emission of 7–10 meV result that the emission bands A_1 (2.557 eV), A_2 (2.520 eV) and A_3 (2.49 eV) may be considered as indirect exciton luminescence annihilation with phonons emission of energies respectively 21, 58 and 88 meV. Such phonon energies were obtained from absorption measurements of modulated light in electric field [29]. Since the binding energy of the indirect electron–hole exciton is ~ 14 meV, results that the cumulative donor and acceptor levels energy due to which photoluminescence emission bands in the blue region of the spectrum are formed is equal respectively to 65 meV (A_2) and 95 meV (A_3).

The band B with maximum at the energy of 2.32 eV ($\lambda = 534$ nm) is dominant in PL spectrum and as shown in Fig. 13.1 has a contour without fine structure which is characteristic for impurity bands [7, 27]. The energy of the band from the green spectrum region depends on the nature and concentration of impurities introduced by doping in the material. In the work of Belenkii and Godzhaev [4] from the analyses of the intensity dependence of the temperature and of the excitation intensity is concluded that this band is formed as donor–acceptor recombination. Further it will be analyzed the PL spectra of *GaS* single crystals doped with *Mn* in order to have additional information about the influence of impurities on the structure of PL spectrum.

The PL spectrum at $T = 80$ K of *GaS* single crystalline blade doped with 1.0 at. %. *Mn* is shown in Fig. 13.2. The luminescence was recorded from the surface (0 0 0 1). The presence of 1.0 at.% *Mn* leads to an attenuation of ~ 2 times of edge luminescence comparing to undoped *GaS* single crystals PL. The dopant (*Mn*) does not modify the structure of edge PL bands, but leads to attenuation to the background level of PL band from the green spectral region (band with maximum at 2.32 eV) as shown in Figs. 13.1 and 13.2. Instead of band B (Fig. 13.1) there is present a new intense PL band in the orange–red spectral region (band C). As shown in Figs. 13.1 and 13.2 the intensity of the band C is at least 90 times greater than the impurity band B. The contour of C band at $T = 80$ K can be decomposed into three elementary Gaussian bands with the maximum energies respectively at 1.870, 1.972 and 2.040 eV.

Fig. 13.3 The PL intensity dependence on excitation with radiation of $\lambda = 337.1$ nm at $T = 80$ K
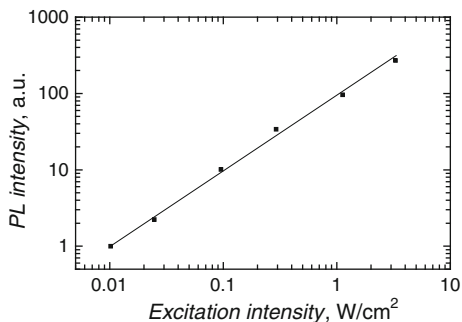
In Fig. 13.3 is presented the PL intensity variation at the temperature 80 K as function of the excitation intensity with the radiation of $\lambda = 337.1$ nm. PL intensity increases linearly with the excitation intensity and satisfy the requirement of monomolecular kinetics [30] characteristic for luminescence centers. It is believed that this band is obtained as a result of electronic transitions in centers of acceptor–vacancy type complexes [5] from analysis of C band contour and PL intensity of temperature.

13.2.2   GaS *Intercalated with* Zn *from Vapor Phase*

The *GaS* single crystal blades intercalated with *Zn* at 753 K leads to changes in the structure of PL spectrum at 80 K. A narrow PL band with maximum at 2.84 eV, a band of low intensity with maximum at 2.48 eV and a intense dominant band with maximum at 2.12 eV is present in the region of the edge of fundamental absorption band of *GaS* crystals as shown in Fig. 13.4. The intercalation of *Zn* atoms between S–Ga–Ga–S packages leads to attenuation of the band with maximum of intensity at 2.32 eV.
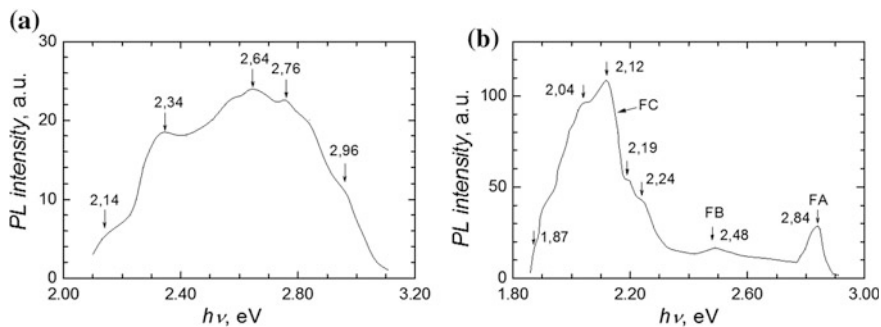

Fig. 13.4 The PL spectra of *GaS* plates heat treated in *Zn* vapor at 753 K for 6 h at: 293 K (**a**) and 80 K (**b**)

The indirect width of bandgap in the undoped *GaS* semiconductor at the temperature of 77 K is equal to 2.591 eV [29]. Four indirect excitons emission bands with phonon emission with maximum intensity at 2570, 2.555, 2.534, 2.521 and 2.480 eV [27] are active in *GaS* doped with *Zn* at *T* = 77 K. As was discussed above, the PL bands at 2.521 and 2.555 eV are also active in the PL spectra of undoped *GaS* single crystals. At the same time, in the crystals doped with *Zn* in an amount of ∼1.0 at.% there is formed a band with dominant intensity in the region of 1.6–2.2 eV and the maximum at 1.85 eV [27].

As is shown in Fig. 13.4 in the PL spectrum at T = 293 K of *GaS* blades intercalated with *Zn* is present a complex emission band located in the spectral region of 1.86–2.30 eV and maximum at ∼2.12 eV. This band is composed of at least five sub-bands with peaks at ∼2.24, 2.19, 2.12, 2.04 and 1.87 eV. Regarding the nature of the particularity at 1.87 eV [27] by measurements of PL intensity variation with temperature and excitation intensity demonstrates the emission mechanism of the center that consists of acceptor–vacancies complexes. The material composed of *ZnS* and *GaS* crystallites are formed as the result of intercalation of *Zn* atoms as was demonstrated by XRD measurements. Thus, the PL band with maximum at 2.84 eV is connected with the presence of *ZnS* crystallites. The structure of PL spectrum for *ZnS* crystals depends on the dopant nature and contains several emission bands that maxima depend on the dopant type.

The width of the direct band gap in *ZnS* crystals at *T* = 80 K is equal to 3.82 eV [31]. The PL spectrum of *ZnS* polycrystals contains a broad band that cover the energy range 2.2–3.0 eV which maximum varies function of the dopant. The maximum of PL band in *Ga*–doped *ZnS* crystals is located at 2.64 eV [32]. Thus, the PL band with maximum at 2.84 eV may be interpreted as a radiative recombination in *ZnS* crystallites from composite. The nature of 2.48 and 2.12 eV bands is related to the recombination processes in *GaS* crystals doped with *Zn*. The PL spectrum of *GaS* crystals doped with *Zn* at 80–100 K is composed of two bands wit peaks at 2.47 and 2.17 eV. The *Ga* vacancies forme three acceptor levels in *GaS* crystals. These vacancies electricaly are in three ionization states V_{Ga}^{+2}, V_{Ga}^{+1} and V_{Ga}^{0}. The *Zn* atoms substitute the *Ga* vacancies in the Zn^{-1} and Zn^0 states to keep electrical neutrality. The emission band with maximum at energy of 2.47 eV in the work of Aono [8] is considered as electronic transition in the complex of *Zn* located in vacancy V_{Ga}^{+2}–donor.

The PL emission band with maximum at the energy of 2.12 eV can be considered as radiative emission of the V_{Ga}^{+2} donor complex—*Zn* acceptor in *GaS* crystals. The substitution of *Ga* vacancy with *Zn* leads to the formation of *Zn*–*S* chemical bond within layered package. At the same time, zinc intercalated between the chalcogenide planes (*S*) of two layered packages at sufficient temperatures forms the valence bond with *S* atoms. Thus, by intercalation of *GaS* with *Zn* from vapor phase are obtained two kinds of luminescent centers one within *S*–*Ga*–*Ga*–*S* elementary packages and other between them.
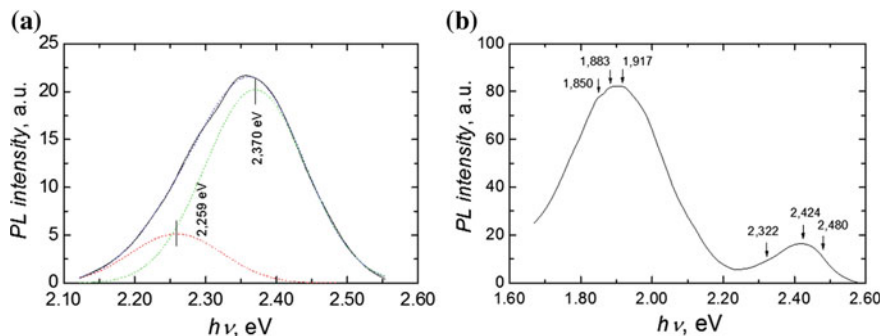
Fig. 13.5 The PL specterum of *GaS* plates heat treated at 753 K in *Cd* vapor for 6 h at: 293 K (**a**) and 80 K (**b**)

### 13.2.3 GaS *Intercalated with* Cd *from Vapor Phase*

The PL spectra at the temperature of 293 K (a) and 80 K (b) of *GaS* single crystalline plates intercalated with *Cd* from the vapor phase at 753 K for 6 h are shown in Fig. 13.5. The PL spectrum at $T = 293$ K is formed by overlapping of two bands with peaks at 2.590 and 2.370 eV. The dominant PL maximum is localized at energy $\sim$ 50 meV lower than the width of direct bandgap of *CdS* compound that is equal to 2.42 eV [33] and it is much smaller than the width of direct bandgap in *GaS*. The resulting PL emission band has no analogue in the PL spectrum of the *GaS* semiconductor. So, we can regard that complex PL band with maximum at the energy of 2.37 eV of *GaS–CdS* micro- and nano-crystalline composite is determined by luminescencent transitions through recombination levels of *CdS* crystallites from composite.

13.3 Photoluminescence of Nanocomposites with *GaSe* Lamellar Semiconductors

The *GaSe* in single crystalline state is among the first materials of chalcogenides class in which has been demonstrated the stimulated emission effect at excitation with accelerated electrons beam [34]. The photoluminescencent emission spectrum from the (0 0 0 1) surface of the *GaSe* single crystalline lamella at the room temperature shown in Fig. 13.6 is obtained by two bands overlaying "A" and "B" with maximum respectively at 2.000 and 1.930 eV.

The binding energy of the electron–hole pair (excitonic Rydberg) is 22 meV. This size is smaller than the thermal energy at room temperature (25 meV). The excitons are strongly ionised at room temperature. During the formation of the edge of the absorption band in *GaSe* crystals at $T = 293$ K together with the direct

Fig. 13.6 The PL spectra at
$T = 293$ K of *GaSe* lamella:
experimental curve (*curve 1*),
experimental curve with
absorption correction (*curve
2*) and curve calculated from
absorption and Van
Roosbroeck-Shockley theory
(*curve 3*)
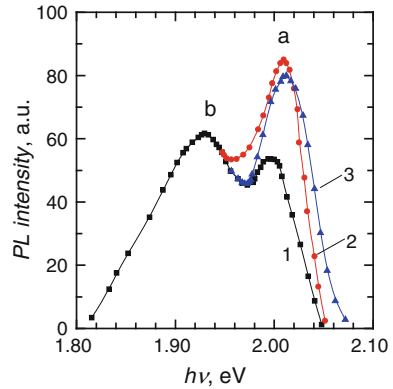
transitions (band–band) the transitions with excitons formation take place. The last
mechanism is even less probable as the sample temperature is higher. Since the
maximum of band "a" (Fig. 13.6) at $T = 293$ K well correlates with the peak of edge
absorption coefficient as well as the broad contour of the band leads to the con-
clusion that the basic mechanism of its formation is band to band recombination in
the center of Brillouin zone.

The growth rate of the absorption coefficient in the edge region of the funda-
mental absorption band of *GaSe* single crystals at $T = 300$ and 80 K is
$\sim 3 \times 10^4$ cm^{-1} eV^{-1}. It was calculated the luminescence spectral dependence of
the band "a" (Fig. 13.6) considering this variation of the edge absorption coefficient
in the edge absorption band region.

The intensity of PL band—I_{PL} band is proportional to radiative recombination
velocity R which according to Van Roosbroeck–Shockley theory is expressed by
the next equality [35]:

$$R = 1.785 \times 10^{22} \left(\frac{T}{300}\right)^4 \int\limits_{u_0}^{\infty} \frac{n^3 \chi u^3 du}{e^u - 1}, \tag{13.2}$$

where n is the refractive index of the luminescent environment; χ–extinction
coefficient; $u = \frac{h\nu}{kT}$; ν–radiation frequency with $u_0 = \frac{E_g}{kT}$.

The PL maximum of "a" band is shifted with ~ 2–10 meV to higher energies
from the maximum of experimental band as it is shown in Fig. 13.6. The difference
between the wing of PL band (Fig. 13.6, curve 2) and those calculated using Van
Roosbroeck–Shockley theory (Fig. 13.6, curve 3) [36] is determined by the pres-
ence of excitonic continuum in this spectral region. The good correlation between
curves 2 and 3 at energies $h\nu < 2.05$ eV (Fig. 13.6) indicates that the PL emission
band "a" with maximum at the energy of 2.00 eV is obtained as a result of
nonequilibrium thermalized charge carrier recombination from the conduction band
(CB) with holes from the valence band (VB) in the center of the Brillouin zone.

Fig. 13.7 The PL spectra of *GaSe* crystals at *T* = 293 K (*curve 1*) and 80 K (*curve 2*)
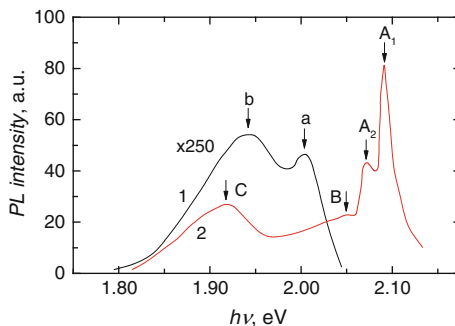
The PL band with maximum at the energy of 1.930 eV is determined by the presence of structural defects and uncontrollable impurities in *GaSe* crystals.

The edge of PL band of *GaSe* lamella shifts to higher energies and the complete restructuration taking place in PL spectrum (Fig. 13.7) when the temperature of sample decrease from 293 to 80 K.

Two narrow bands (A_1 and A_2) with maximum at the energy respectively of 2.092, 2.072 eV and a plateau C with maximum at energy 1.920 eV are present in the edge region of absorption band. The band A_1 at the temperature of 80 K is shifted by $\sim$6 meV toward low energies from the absorption line of free excitons in state n = 1. This shift is much smaller than the energy of phonons that are active in photoluminescence emission (15 meV) [12]. It can be considered that the band A_1 is obtained as a result of luminescent annihilation of direct exciton in n = 1 state localized at the acceptor with binding energy of 6 meV. The band B that is shifted by 20 meV from the band A can be considered as phononic repetition of line A of localized direct excitons.

The phonon with the energy of $\sim$20 meV is emitted in the emission process of B band. Note that the phonon with energy of $\sim$18.8 meV corresponds to the vibration of *Se–Ga–Ga–Se* packages one to another [37]. The elemental cell of *ε-GaSe* modification consists of three elementary packings that are displaced one from each other by 1/3 *a* [38]. The plateau C (2.050 eV) in Capozzi and Minafra [12] is interpreted as luminescent emission of indirect exciton in the M point of Brillouin zone with the emission of phonon with the energy of 13 meV.

The band B with maximum at the energy of 1.920 eV is highlighted in the PL spectra at low excitation intensities of undoped *GaSe* crystals. The relative intensity of this PL band depends on the temperature as an exponential function of the $I_{FL} \sim exp \frac{\Delta E}{kT}$ type. At the same time, the intensity of B band depends on the dopants and increases with the *Cu* concentration and it is interpreted as radiative electron transition in the VB from the deep donor level with energy 1.92 meV from the CB.

The PL spectrum of the *CdSe* polycrystalline compound at 300 and 78 K consists of the intense band with maximum in the edge region of absorption band (Fig. 13.8). As shown in Fig. 13.8, curve a, the maximum of PL band of *CdSe* compound at *T* = 293 K is situated at the energy of 1.72 eV. This result well

Fig. 13.8 The PL spectra of *CdSe* compound at 293 K (*curve a*) and 80 K (*curve b*)
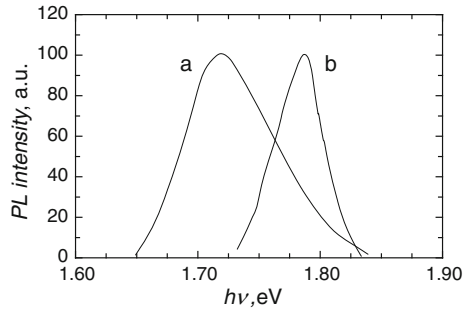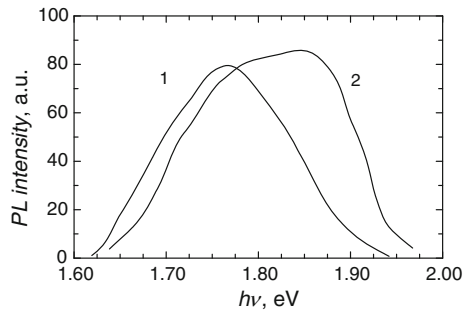

Fig. 13.9 The PL spectra of *GaSe–CdSe* composite obtained by *GaSe* plates heat treated at 833 K in *Cd* vapor for 20 h at: 293 K (*curve 1*) and 80 K (*curve 2*)


correlates with PL spectrum from the surface of the *GaSe* that was heat treated in *Cd* vapor (Fig. 13.9, curve a). Additional information on the composition of the formations on the *GaSe* plates surface that was heat treated in *Cd* vapor (*GaSe–CdSe* composite) can be obtained from the analysis of PL spectra at the temperature of 293 and 80 K (Fig. 13.9). The photoluminescence was excited by radiation of N_2 laser ($\lambda = 337.4$ nm) with energy of 3.67 eV.

As can be seen from the comparison of Figs. 13.8 and 13.9, the PL spectrum of composite at room temperature contains the PL spectrum of the *CdSe* compound and two bands, one at ~ 1.65 eV with low intensity and the second more intense with a maximum in the region of 1.80 eV. The decreasing of the intensities of component bands occurs when the intensity of the emission band of *CdSe* crystallites from composite increasing. The nature of bands at 1.65 and 1.80 eV is probably determined by restructuration of diagram of recombination levels in the *GaSe* crystallites as result of crystal micro-structuration and the formation of new luminescencent recombination levels. The PL spectrum of *CdSe–GaSe* composite obtained at 853 K (Fig. 13.10) can be decomposed into four Gaussian curves with maxima at energies 1.78 eV (A), 1.73 eV (B), 1.71 eV (C) and 1.68 eV (D).

The probability of excitons formation is small and respectively their contribution to the formation of PL emission band at room temperature is small. Thus, the curves B and C can be caused respectively by band to band recombination and recombination that involve low energy acceptors (~ 20 meV) from VB in *CdSe*. The A

Fig. 13.10 The PL spectrum at 293 K of *GaSe–CdSe* composite obtained by heat treatment at 853 K of *GaSe* plates in *Cd* vapor
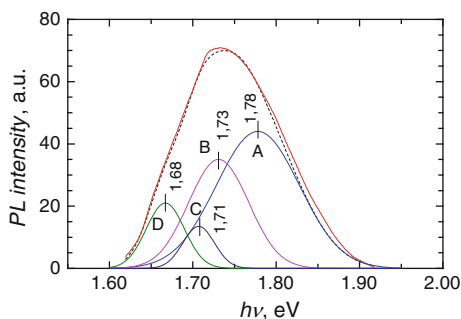
band having lower energy than the width of bandgap in *CdSe* semiconductor allows to admit that it is donor–acceptor type recombination in *GaSe* crystallites. It is known that as a result of the heat treatment at the temperature of ∼800 K and higher in *GaSe* crystals are formed structural defects by the accumulation of *Se* atoms between elementary *Se–Ga–Ga–Se* packages and creates *Se* vacancies in their atomic planes. These defects form deep acceptor levels that are located at 0.45 eV from VB. The CB–deep acceptor recombination in the *GaSe* crystallites of the composite may cause the luminescence in the region of D curve. The forming process of the *CdSe–GaSe* composite occurs with *Ga–Se* bonds breaking. The *Ga* atoms at heat treatment temperature of ∼853 K are doping the new formed *CdSe* crystallites and *GaSe* crystallites. The *Ga* atoms interstitially arranged form deep donor levels [16] and PL band A is obtained as a result of transition from this donor level on the acceptor level in *GaSe*.

The PL edge band at $T = 80$ K of *CdSe–GaSe* composite obtained by *GaSe* plates that was heat treated at 853 K in *Cd* vapor is formed by the band "a" (Fig. 13.11) with maximum at the evergy of 1.880 eV. The PL band with maximum at the energy of 1.870 eV were found in the PL spectra of undoped *GaSe* crystals and in PL spectrum of *GaSe* crystals doped with ∼10^{18} cm^{-3} of copper there are highlighted lines with maximum at 1.870 and 1.890 eV [12]. The *Cd* as a dopant in small amounts forms in the bandgap of *GaSe* crystals acceptor levels with energy from 0.26 to 0.30 eV from VB. Since the band "a" from Fig. 13.11 is found at the

Fig. 13.11 The PL spectrum at $T = 80$ K of *GaSe–CdSe* composite obtained by *GaSe* plates heat treatment at 853 K in *Cd* vapor
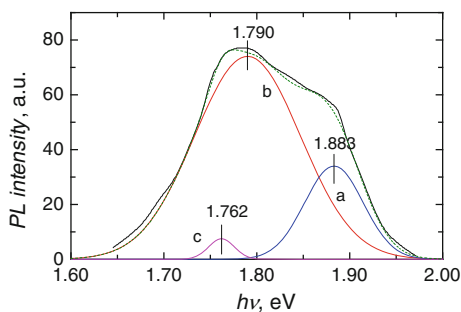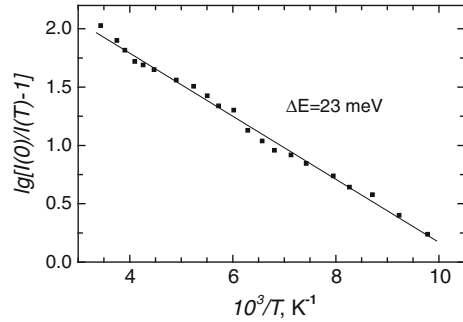
Fig. 13.12 The energy of PL thermal activation for *GaSe* lamella intercalated with *Cd*

energy greater than the width of bandgap in *CdSe* at $T = 80$ K, it can be obtained as a result of nonequilibrium radiative transition of electrons from CB to the acceptor level with the energy of 0.24 eV from VB of *GaSe* crystallites from composite.

The intensity of PL band with the maximum at 1.790 eV decreases monotonous when the temperature of intercalation process of *GaSe* with *Cd* from 80 to 293 K. The dependence of PL intensity (I_{PL}) on temperature in the temperatures range of 78–293 K as shown in Fig. 13.12 is well described by the expression [39]:

$$I_L = \frac{I_0}{1 + A \exp\left[-\frac{E_T}{kT}\right]}, \tag{13.3}$$

where I_0 is the PL intensity extrapolated to 0 K, E_T–PL thermal activation energy, A–the ratio of the probabilities of emisional and non–emisional transitions, k–Boltzmann constant.

There is observed a good coincidence of the respective bands maxima at 78 and 293 K by comparing the PL spectra of *GaSe* crystals intercalated with *Cd* at 823 K for 6 and 24 h. At the same time, the PL bands of both primary *GaSe* crystals and *Cd* intercalated *GaSe* crystals are identical at high energies. So we can admit that *Cd* atoms in vapor phase at 823–853 K probably intercalate between *Se* atoms planes within *Se–Ga–Ga–Se* layered packages and forming *CdSe* layers. This conclusion is argued and by the fact that at doping with *Cd* (concentration of 0.01–0.10 at.%) in the synthesis process of *GaSe*, the *Cd* atoms form deep acceptor levels at 0.26–0.28 eV [40]. Thermal activation energy of impurity bands present in luminescent emission spectra of *GaSe* crystals doped with *Cd* also has a magnitude of hundreds meV (130–370 meV) [41]. At thermal quenching of photoluminescence of *GaSe* intercalated with *Cd* is obtained the activation energy of 23 meV.

Much more pronounced highlights the complex structure of PL spectrum at 80 K (Fig. 13.9). The spectrum of *CdSe–GaSe* micro-composite at this temperature contains edge emission band of *CdSe* crystallites with the maximum at the energy of 1.79 eV, a medium intensity band in the energy range of 1.65–1.75 eV and a band localized at higher energy with maximum in the range of 1.85–1.95 eV. The intensity of PL band localized at higher energies increase and the intensity of the band localized at lower energies than PL band of *CdSe* crystallites decreases when

Fig. 13.13 The PL spectrum at T = 78 K of *GaSe* crystals doped with 0.05 at.% *Cd*
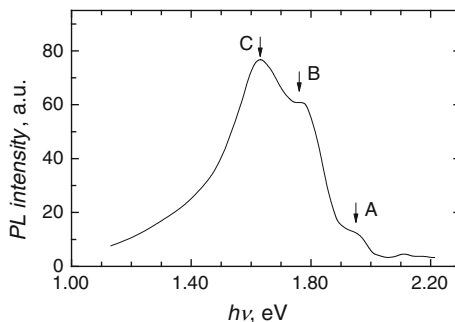
the temperature of heat treatment decrease from 883 to 853 K. This dynamic of the structure of PL spectra can be explained if we admit that the PL band from high energy region is determined by radiative processes in *GaSe* crystallites probably doped with *Cd* and *Ga* from composite.

It is known [41] that by *Cd* doping of *GaSe* crystal in the concentrations range of 0.05–0.10 at.% the PL spectrum suffers cardinal changes. If in undoped *GaSe* crystals the PL spectrum contains direct exciton annihilation line in the state n = 1 by 2.10 eV energy band emission and LO phonon repetition of indirect luminescent recombination from CB in point M of Brillouin zone, then 0.01 at.% concentrations of *Cd* atoms in *GaSe* occurs the attenuation of edge line intensity and formation of two other bands. In the PL spectrum of the *GaSe*: 0.01 at.% *Cd* compound is present a dominant band with maximum at energy 1.95 eV and a much smaller intensity band with maximum at 1.60–1.65 eV. The intensity of this band increases when the concentration of the dopant increase and at 0.10 at.% concentration it becomes the dominant band. The PL spectrum contains three bands: a low intensity band (A) with peak at the energy of 1.95 eV and two intense bands with maxima at 1.75 eV (B) and 1.62 eV (C) for *Cd* atoms concentration of 0.05 at.% in *GaSe*. The wing of C band covers the range of energies up to ∼1.1 eV (Fig. 13.13) [41].

Note that the PL emission bands at T = 80 K are also obtained in *GaSe* crystals doped with 0.05 at.% *Ag* [42]. The excess of *Ga* atoms form deep donor and acceptor levels in the *GaSe* semiconductor band gap. Through 0.152 eV acceptor level and 0.175 eV donor level occurs the donor–acceptor band PL emission with maximum at 1.77 eV [16]. As shown in Fig. 13.11, the PL spectrum of the *GaSe*–*CdSe* composite obtained by *GaSe* plates treatment in *Cd* vapor at 853 K, well decompose in three Gaussian curves (a, b, and c) with maxima at energies respectively 1.883, 1.790 and 1.762 eV.

Good coincidence of the PL spectrum at 80 K of *CdSe* compound (Fig. 13.8a) with the curve *b* with the maximum at the energy of 1.790 eV from Fig. 13.11 it is an additional confirmation of the presence of *CdSe* crystallites in the composite. The *c* curve from Fig. 13.11 correlates well energetically with the luminescent emission band present in *GaSe* crystals doped with 0.05 at.% *Cd* (Fig. 13.13). The presence of band in the PL spectrum is determined by a certain concentration of *Cd* atoms in the sample because at *Cd* concentrations of 0.01 and 0.10 at.% this band is

missing [41]. The nature of C band finds interpretation if we admit that in *Cd* doped *GaSe* crystals at the same time with two acceptor levels localized at 0.10–0.13 eV from VB there is formed a donor level at 0.36 eV from CB. The luminescence emission band with maximum at 1.762 eV is obtained as a result of electrons transition in VB from the donor level with energy of 0.36 eV from CB.

The treatment temperature and its duration are the factors that determine the size of the *CdSe* crystallites, both on the outer surface and at the interface between the *Se–Ga–Ga–Se* elementary packages. The modification of PL spectra function of these two technological parameters will be analysed. In Fig. 13.14a, b are presented PL spectra at the temperature of respectively 293 and 80 K for the *GaSe–CdSe* composite obtained by heat treatment of *GaSe* plates in *Cd* vapor at 793 K for 6 h. The PL spectra at 293 K of the composites obtained respectively at the temperature of 853 and 793 K have identical form as it was shown in Figs. 13.14a and 13.9. Thus the material composition and the diagram of energy levels through which the radiative electronic transitions occur does not substantially changes at the reduction of heat treatment temperature of ~60 K and the length of the process from 24 to 6 h.

More pronounced differencies are present between PL spectra measured at 80 K (Fig. 13.14b). As shown in Fig. 13.14b the PL spectrum at T = 80 K is composed of an intense band (A) with the maximum at ~1.837 eV and a low intensity structured band (B) in the region of 2.1–2.8 eV with the maximum of intensity at the energy of 2.478 eV. The band A can be decomposed into two Gaussian curves with a maxima at 1.76 and 1.85 eV. The band with maximum at the energy of 1.76 eV is present in the PL spectrum of *GaSe–CdSe* composite obtained at the temperature of 853 K (Fig. 13.11, curve c).

The PL band (Fig. 13.14b, the curve B) covers a wide range of energies and it can be decomposed into four elementary curves (Gaussian) with the peaks at the energies of 2.300, 2.478, 2.660 and 2.776 eV. This PL band lies at higher energies than the width of bandgap of *GaSe* (2.120 eV) and *CdSe* (1.792 eV) crystallites. A qualitative interpretation of the nature of this band (Fig. 13.14b, the curve B) can be found if we admit that the composite contains both *GaSe* and *CdSe* crystallites with micro and nano dimensions. The presence of nanoparticles with sizes of
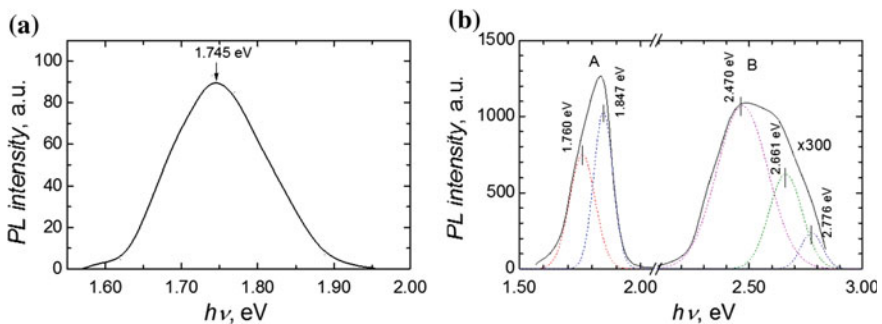

Fig. 13.14 The PL spectra of *GaSe–CdSe* composite obtained by *GaSe* plates heat treatment at 793 K in *Cd* vapor for 6 h at: 293 K (**a**) and 80 K (**b**)
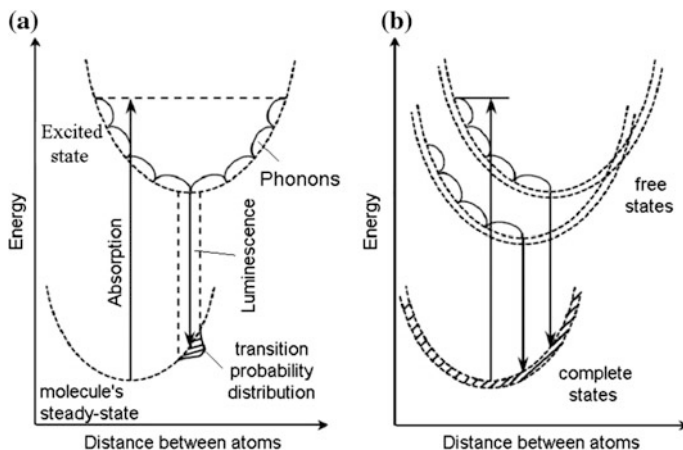
Fig. 13.15 The energetic diagram of diatomic molecule (**a**) and nanocrystal (**b**)

10–20 nm in researched *GaSe–CdSe* composites was demonstrated by XRD diffraction line contour analysis.

The PL spectrum of *CdSe* composites consisting of nanoparticles in various inorganic and organic solutions is shifted to the green region of the spectrum [43]. The PL spectrum of *CdSe* quantum dots with diameters in the range of 1.40–1.82 nm covers the energy range of 1.7–3.0 eV with broad peak at $\sim$2.3 eV. The PL band maximum at $T = 293$ K for *CdSe* quantum dots varies in a wide range of energies 2.14–2.60 eV and it depends on the size of the nanoparticles (3.0–10.0 nm) [44]. However in Boatman [44] is mentioned that the PL intensity depends on obtaining technology of *CdSe* structures.

The *CdSe* nanoparticles into semiconductor matrix are promising materials for light sources in blue–green region of the spectrum with low excitation energy loss [45]. The *CdSe* quantum dots at excitation with photon energy of $hv \geq 3.0$ eV emit radiation in the green region of the spectrum. The emission band at $T = 80$ K PL shifts in the blue region of the spectrum (2.5–2.6 eV). The PL maxima of nanostructures based on nanoscale *CdSe* layers are effective violet radiation sources. The maximum of luminescence band of nano-structure with *CdSe* films on the *ZnSe* layer is at 2.57 eV [45].

The PL spectrum of *GaSe–CdSe* composite at both room and low temperature ($T = 80$ K) was excited with the radiation of N_2 laser ($\lambda = 337.4$ nm) with the energy of 3.67 eV and it is much higher than the energy of PL bands. The absorption spectra and simple contour of PL bands of nanometric composites are interpreted using the approximation of configurational diagrams [46] analogically with absorption and emission processes in molecules (luminescence centers in crystals) (Fig. 13.15a) and semiconductor nanocomposites (Fig. 13.15b).

The composite's PL bands contour shape finds explanation based on the Frank–Condon principle. The probability of electronic transitions $W_{v'v''}$ of *CdSe* molecule/quantum point from the excited state (n′v′) in the basic state (n″v″) is equal to the square of the overlap integral [47]:

$$W_{v'v''} = C \left| \int \psi'_{v'}(\rho) \psi''_{v''}(\rho) d\rho \right|^2, \tag{13.4}$$

where C is a constant, v' and v'' are the vibrational quantum numbers respectively of excited electronic state and the basic state, $\psi'_{v'}(\rho)$ and $\psi''_{v''}(\rho)$ are the vibrational wave functions of respectively the excited electronic state and the basic state of nanoparticles. Therefore, the PL subbands of the *GaSe–CdSe* composite with peaks at 2.32, 2.48 and 2.62 eV, can be obtained if we admit that as a result of the *GaSe* plates treatment in *Cd* vapor at 793 K temperature for 6 h are obtained the *CdSe* microcrystalline with PL spectrum of in the range of 1.79 eV and three types of *CdSe* nanocrystallites with sizes from units to tens of nm. We'll analyze the PL of *GaSe* plates that were heat treated in *Cd* vapor for 10–100 min. In Fig. 13.16 is shown the PL spectrum at $T = 293$ K (a) and 80 K (b) of the composite obtained by treatment at 823 K for 10 min. The PL spectrum at $T = 293$ K (Fig. 13.16a) is located at energies $hv \le E_g$ (*GaSe*) and is composed of at least three bands with peaks at 1.99, 1.97 and ~1.95 eV. The PL band with maximum at 1.99 eV is obtained by overlay of PL spectra of electronic transitions from CB in the maximum of VB in the center of Brillouin and the emission band of direct excitons annihilation in *GaSe*. The particularity "a" finds interpretation as phonon repetition of the band of direct excitons with phonon emission that have the energy of ~20 meV. The particularity "b" may be associated to radiative emission at indirect electronic transitions (M–Γ) with phonon emission that has the energy of 15 meV. The contribution of phonon with the energy of 15 meV in the PL spectrum of *GaSe* compound it is demonstrated in several works including Abdullaev [48]. Two new particularities apears in the PL spectrum at $T = 80$ K (Fig. 13.16b)—one impurity
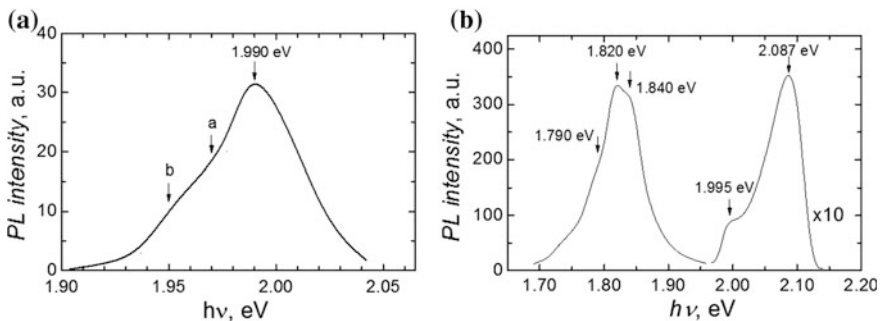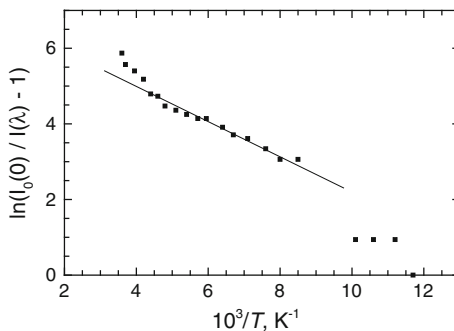

Fig. 13.16 The PL spectra of *GaSe* plates heat treated at 823 K in *Cd* vapor for 10 min at: $T = 293$ K (**a**) and 80 K (**b**)

Fig. 13.17 Thermal
quenching of PL band with
maximum at the energy of
2.087 eV

band with absolute maximum at the energy of 1.820 eV and the edge band with maximum at 2.087 eV. The band with maximum at 2.087 eV can be interpreted as radiative emission of direct excitons located at ionized acceptor. The energy of acceptors that was formed by own structural defects in *GaSe* has values of ~ 0.11 and 0.13 eV while the energy range between the width of direct bandgap of *GaSe* at $T = 80$ K (2.120 eV) and the energy of the edge band (Fig. 13.16b) is only 33 meV. In order to interpret this band was studied the inverse temperature dependence of its intensity (Fig. 13.17).

From this graph can be well seen that thermal quenching of the band 2.087 eV is well described by function (13.3). Thermal activation energy at low temperatures (for $10^3/T$ in the range of 8–11) is equal to 55 meV, and in the average temperatures range of 125–250 K) the photoluminescence thermal activation energy is equal to 33 meV. It follows that the PL emission band with maximum at 2.087 eV is obtained as a result of electron transitions from CB on an acceptor level located at 33 meV from the CB in the center of Brillouin zone. The band at 1.955 eV [14] is associated to electronic transition CB–acceptor level with the energy of 0.093 eV and it is formed by *Cd* as dopant in *GaSe*. The structural defects and respectively acceptor and donor deep energy levels are formed by the heat treatment at high temperatures due to movements of elementary packages. Simultaneously with the formation of *CdSe* compound, the *Ga* atoms surplus is formed. A part of them forms metallic clusters and defects in *GaSe* crystallites lattice and probably *CdSe*. The *Ga* surplus in the work of Shigetomi [16] is assigned to the formation of donor level 0.175 eV and acceptor level 0.152 eV that are active in the process of luminescent recombination. Thus, the PL band from energies region of 1.840 eV is obtained as the result of donor–acceptor electronic transitions with the participation of donor level formed by the surplus of *Ga* atoms in *GaSe* crystallites with the energy of 0.175 eV and acceptor level with the energy of 0.100 eV.

The band at 1.820 eV can be considered as a result of overlapping of the band 1.840 eV and the edge luminescence band in *CdSe* crystallites with the maximum at the energy of 1.790 eV. A pronounced change in the PL structure at $T = 293$ K is observed when the duration of heat treatment increases from 10 to 40 min (Fig. 13.18a).
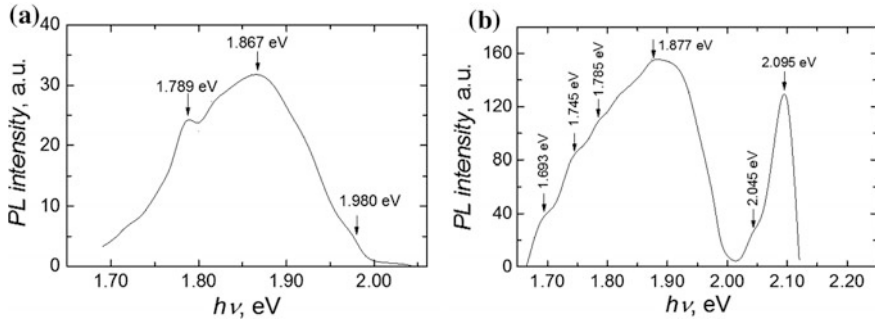
Fig. 13.18 The PL spectra of *GaSe* plates heat treated at 823 K in *Cd* vapor for 40 min at: *T* = 293 K (**a**) and 80 K (**b**)

The PL intensity decreases substantially for CB–VB recombination band (maximum 1.99 eV). The band at energy of 1.867 eV increases and a band at the energy of 1.789 eV is clearly highlighted. These two bands are obtained as a result of luminescent emission overlay in *GaSe* and *CdSe* crystallites from composite. The PL spectrum at *T* = 80 K (Fig. 13.18b) of the composite obtained by heat treatment at 823 K for 40 min is composed of direct exciton emission band with maximum at 2.095 eV. The PL band with maximum at 2.045 eV is attributed to luminescent recombination through indirect excitons. The PL band with maximum at 1.877 eV is associated to donor–acceptor type transitions in *GaSe* crystals with *Ga* surplus also with the participation of deep donor levels with the energy of 0.175 eV and an acceptor level with the energy of ~50–60 meV. The structure with three thresholds at the energies of 1.693, 1.745 and 1.785 eV probably is obtained as the result of impurity bands overlapping in *GaSe* crystallites with edge emission band of *CdSe* crystallites (1.790 eV) from composite.

The *GaSe–CdSe* composite was subjected to short heat treatment for ~20 min in oxygen atmosphere in order to determine the nature of the 1.877 eV band. As it can be seen from the comparison of Figs. 13.18a, 13.19a the treatment in oxygen leads to the extinction of 1.98 eV band. Also, the dominant bands remain at the energies of 1.87 and 1.79 eV and two additional bands at 1.742 and 1.69 eV appear. As can be seen from the comparison of Figs. 13.18b, 13.19b the oxygen presence in the composite influences on energy levels diagram located in the bandgap of *GaSe* compound. Thus, the attenuation of impurity band with maximum at 1.877 eV and shaping of edge emission band in *CdSe* crystallites from composite take place (1.790 eV band amplifies). At the same time, the oxygen creates donor energy levels at 0.256, 0.330 and 0.41 eV from the CB minimum. The emission bands with maxima at 1.734, 1.664 and 1.575 eV are considered the PL emission of donor–acceptor type with participation of acceptor level of 0.13 eV.

The increasing of heat treatment duration up to 100 min changes the structure of PL spectrum in temperature range from 80 to 290 K. Thus, as the result of *Cd* intercalation in *GaSe* crystals occurs shielding of the electron–hole (excitons) bonds
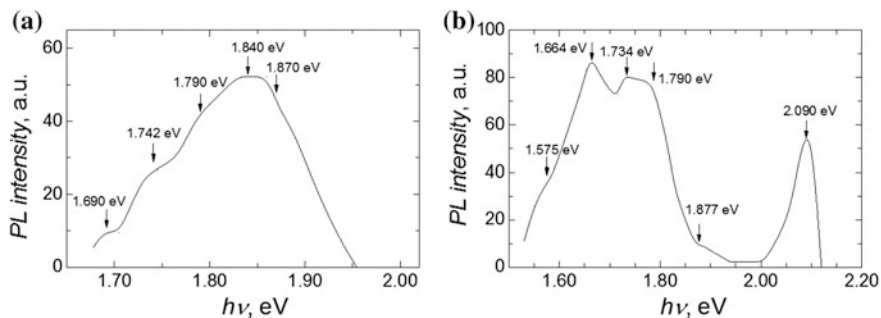
Fig. 13.19 The PL spectra of *GaSe–CdSe* composite obtained by heat treatment at 823 K of *GaSe* plates in *Cd* vapor for 40 min and heat treated for 20 min. in oxygen atmosphere at: *T* = 293 K (**a**) and 80 K (**b**)

in the whole temperature range. At the same time, in the plates intercalated for 40 min the donor–acceptor band with maximum at 1.88 eV shifts toward to low energies.

The plateau at the energy of 1.79 eV together with PL band with maximum at the energy of 1.848 eV clearly highlights in Fig. 13.20a. This peculiarity's energy coincides with the energy of maximum PL band in polycrystalline *CdSe* layers and it is considered as donor–acceptor luminescence in *CdSe* crystals.

In Fig. 13.21 are shown the temperature dependences of the n = 1 exciton energy (a) and the maximum of PL band of the *GaSe* semiconductor (b). The linear decrease of occurs the band with the energy of 1.848 eV and it's shift toward low energies (Fig. 13.21b) occurs when the temperature increase from 80 to 293 K. The good coincidence of the dependency $E_{n=1}(T)$ and the maximum at the energy of 1.848 eV (*T* = 80 K) indicates that this band can be considered as luminescent recombination from CB on acceptor level.

To establish the minimum temperature of composite *CdSe–GaSe* obtaining were prepared samples at the temperature of 753 and 773 K. In Fig. 13.20 is shown the
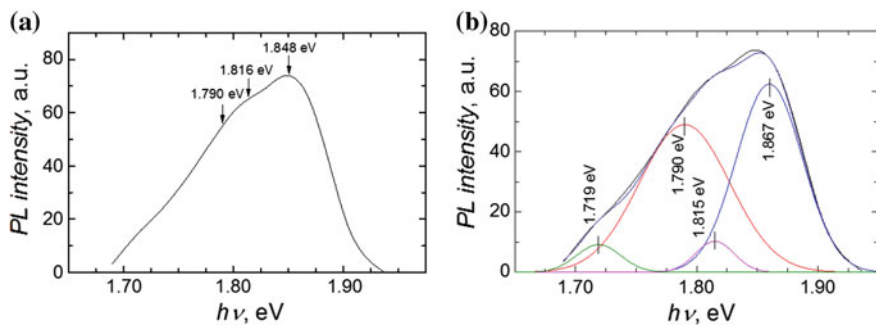

Fig. 13.20 The PL spectrum at *T* = 80 K of *GaSe* plates heat treated at 773 K in *Cd* vapor for 100 min
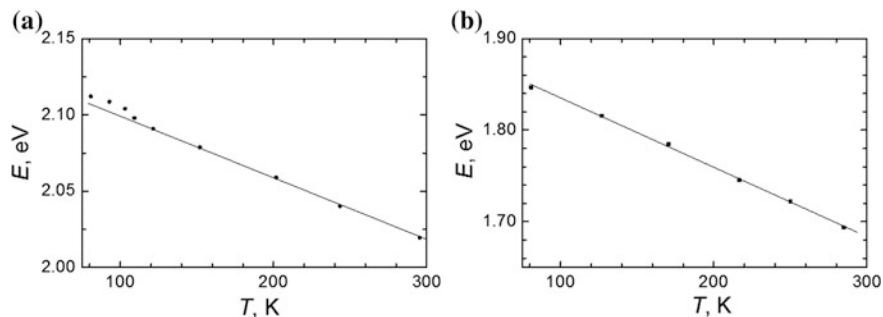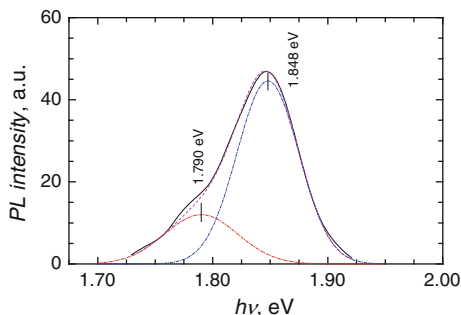
Fig. 13.21 The temperature dependence of n = 1 exciton energy (**a**) and PL band with maximum at 1.848 eV of *GaSe* plates heat treated at 773 K in *Cd* vapor for 100 min

Fig. 13.22 The PL spectrum at T = 80 K of *GaSe* plates heat treated at 753 K in *Cd* vapor for 6 h

PL spectrum at T = 80 K of this sample (773 K). The PL spectrum consists of four bands with peaks at energies 1.867, 1.815, 1.790 and 1.720 eV. These PL bands are obtained as a result of PL overlapping of the impurity luminescence band of *GaSe* crystallite and the edge band with maximum at 1.79 eV of *CdSe* crystallites from composite. The PL spectrum of the composite obtained at 753 K and treated in *Cd* vapors for 6 h is presented in Fig. 13.22. The emission band of this sample at T = 80 K covers the energy range of $\sim$1.70–1.92 eV and has the maximum at 1.847 eV. The impurity emission band in *GaSe* crystallites (1.847 eV) and the plateau is highlighted. It is energy well correlates with the maximum of PL emission band at this temperature of *CdSe* polycrystals.

The structure of *GaSe* layered crystalline compound determines the anisotropy density of surface states in perpendicular and parallel planes to the C_6 crystallographic axis. If the density of free valence bonds on the surface (0 0 0 1) of *GaSe* single crystalline plates is $\sim 10^{10}$ cm^{-2}, then the density of free bonds exceeds 10^{20} cm^{-2} on the surface (0 1 0 0). The possibility to obtain *CdSe* crystallites by heat treatment of *GaSe* crystals in *Cd* vapor was analyzed through PL spectra of *CdSe–GaSe* composite (Fig. 13.23). The *GaSe* poweder with mean particle size

Fig. 13.23 The PL spectrum at $T = 80$ K of compound obtained by the mixture of *GaSe* and *Cd* powders that was heat treated at 573 K in vacuum for 3 h
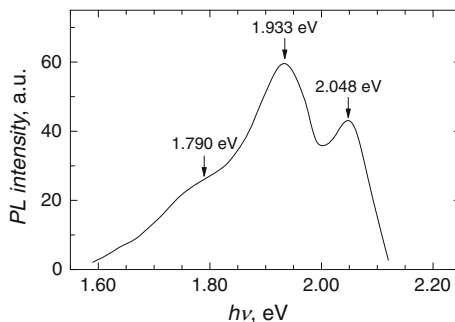

of $\sim$1–10 μm that was mixed with *Cd* powder (Ø = 1–5 μm) was used to obtain the samples. The mixture was subjected to heat treatment at $\sim$573 K in vacuum for 3 h.

There are various methods of metal intercalation in layered materials including most commonly the electrochemical intercalation from solutions. In Fig. 13.24 is shown the PL spectrum at $T = 80$ K of *GaSe* plate intercalated with *Cd* ions from the $CdCl_2$ aqueous solution of 10 % concentration.

The *Cd* ions intercalation occurred at the current density of 30 mA/cm^2 for 45 min. After electrolytical intercalation the sample was subjected to heat treatment in vacuum at 753 K for 40 min. The PL spectrum at $T = 80$ K presents a wide emission band with strongly asymmetrical contour and maximum at the energy of 2.047 eV. The *Cd* dopant in *GaSe* forms two acceptor levels, with energies of 0.28 and 0.13 eV from the valence band [15]. The accumulation of $CdCl_2$ molecules and *Cd* ions occurs between the layers because of the weak bonds between the elementary packages in electric field. Thus, the doping of *GaSe* semiconductor with *Cd* and Cl occurs at the heat treatment at 753 K of *GaSe* samples intercalated with *Cd* and $CdCl_2$. The heat treatment was performed in $\sim$5 × 10^{-5} mm *Hg* vacuum or the evacuation of $CdCl_2$ molecules from *GaSe* plates. The *Cl* atoms formes donor levels in the *GaSe* bandgap at the energies of 0.38, 0.56, 0.57 and 0.62 eV [49, 50] and acceptor levels at 0.2 eV from the VB. As it was mentioned above, the *Cd* as dopant formes in the *GaSe* bandgap an acceptor level at 0.13 eV from VB and a deep donor level at 0.37 eV from CB. The particularity of PL spectrum at the

Fig. 13.24 The PL spectrum at $T = 78$ K, of *GaSe* plate intercalated with *Cd* ions from $CdCl_2$ aqueous solutions and heat treated at 753 K in *Cd* vapor for 40 min
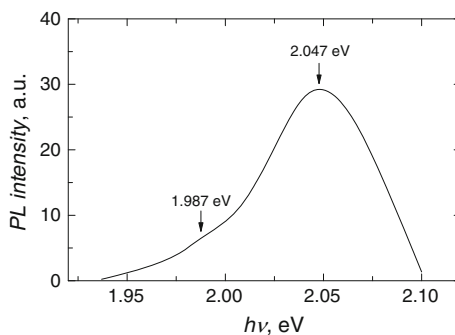
energy of 1.987 eV can be interpreted as electronic transition from CB minimum in the center of the Brillouin zone onto acceptor level (0.13 eV). This conclusion was done taking into account the diagram of the energy levels formed by *Cd* and *Cl* as a dopant in *GaSe*. The wide PL band with the maximum at the energy of 2.047 eV is obtained as a result of overlapping of unionized indirect exciton emission bands and low energy phonons emission (10–15 meV).

The intercalation of *Cd* ions and *CdCl$_2$* molecules leads to the deformation of crystal lattice, particularly on the C$_6$ axis direction which is manifested by shielding of exciton links in the center of Brillouin zone and complete attenuation of the radiative annihilation of PL band of these excitons. This band is well pronounced in the PL spectra of *CdSe–GaSe* composites obtained from the vapor phase.

13.4 Photoluminescence of Nanocomposites with *GaTe* Lamellar Semiconductors

The physical and chemical properties of materials are determined by their electronic states. The materials with cardinally new properties are obtained by doping and intercalation of semiconductors. As the result the filling of energy levels occurs [51]. The characteristics of materials, and especially the electronic states, are well evidenced by absorption and emission measurements of radiation close to bandgap of materials.

The PL spectrum at $T = 78$ K of *GaTe* plate excited with the radiation of *He–Ne* laser ($\lambda = 632.8$ nm, $P = 5$ mW) contains a narrow peak at 1.770 eV and a low intensity band with poor shaped maximum at ~ 1.68 eV (Fig. 13.25a). The maximum of dominant band coincides with the state n = 1 of direct excitons absorption line [52] and can be considered as radiative annihilation of excitons. The PL band from 1.63 to 1.75 eV has an impurity nature, including structural defects that can be caused by the movements of *Te–Ga–Ga–Te* elementary packages. The intensity of this band decreases down to the fund level as the result of long-term treatment (60–80 h) in an inert atmosphere (*Ar*) at 673–693 K.

The PL spectra at $T = 80$ K of the composites obtained by heat treatment of *GaTe* plates in *Cd* vapor at 653 K for 60 h and 833 K for 24 h are shown in Fig. 13.25b, c. The PL spectrum of composite obtained *GaTe* plates that were splitted from single crystals and kept in normal atmosphere for 3 years then treated in *Cd* vapor at the temperature of 653 K for 60 h (Fig. 13.25d).

The contour of PL spectrum at 78 K of the composites obtained from *GaTe* plates that was heat treated in *Cd* vapor at the temperature of 653 K for 60 h well decomposes into three Gaussian curves with maxima at 1.460, 1.402 and 1.372 eV (Fig. 13.25b). The band with maximum at 1.460 eV is interpreted as luminescent recombination through states formed by structural defects and particulary by *Cd* vacancies in *CdTe* [53, 54]. The band at 1.372 eV is well studied in the work of
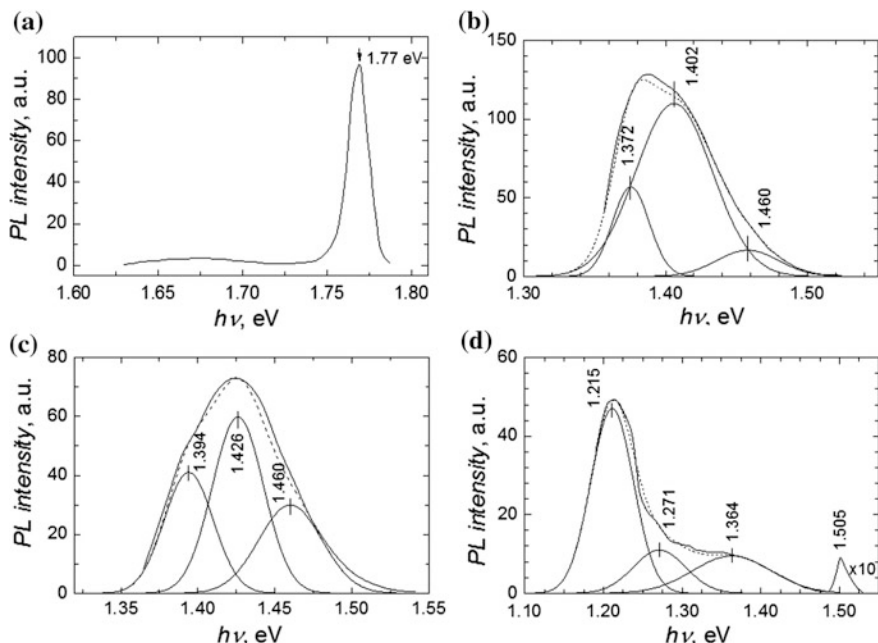
Fig. 13.25 The PL spectra at $T = 80$ K of *GaTe* plate (**a**) and composites obtained by heat treatment at: 653 K of *GaTe* plates in *Cd* vapor for 60 h (**b**), 833 K for 24 h and (**c**) 653 K temperature for 60 h in *Cd* vapor and kept in atmosphere for 3 years

Vatavu [55] and is interpreted as donor–acceptor radiative emission. The band with the maximum at 1.402 eV probably also has a donor–acceptor nature.

The increase of the temperature of heat treatment from 653 to 833 K leads to the shift of the maximum of PL band from 1.387 to 1.427 eV (Fig. 13.25c). This band is well decomposed into three Gaussian curves with peaks at 1.460, 1.426 and 1.394 eV. As shown in Fig. 13.25b, c the relative intensity of the band with the maximum at 1.460 eV increase compared to component sub–bands from 1.426 and 1.394 eV. This fact indicates an increase in structural defects in metal sublattice of the *CdTe* crystallites from composite. More pronounced changes occurs in the structure of PL spectrum of the composite obtained from *GaTe* plates splitted from *GaTe* single crystals that was kept for 3 years in normal atmosphere (Fig. 13.25d). This composite PL spectrum covers the range of energies from 1.12 to 1.52 eV with absolute maximum at 1215 eV. In this spectrum a low intensity band highlights at 1.505 eV. Note that the presence of this band and the shift of dominant PL band toward low energy region are characteristic of *CdTe* films obtained in oxygen enriched atmosphere [56]. We can admit that as a result of keeping the *GaTe* crystals in the normal atmosphere it took place an oxygen intercalation between *Te–Ga–Ga–Te* layered packages. The oxygen presence contributes to valence bonds formation with its closest *Te* atoms and forms TeO_2 oxide. The TeO_2 impurities in

Fig. 13.26 The dependence
of PL peak intensity on the
reciprocal temperature for
GaTe single
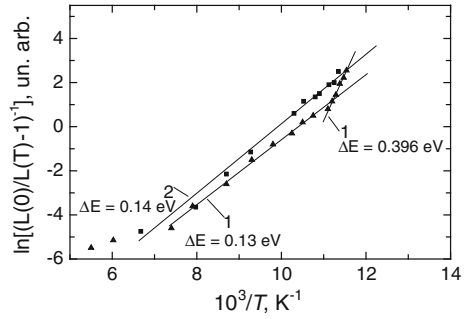
CdTe form an emission band in the range of 1.20–1.30 eV and also attenuates the
PL band with peak at 1.42 eV as shown in Augelli [57]. As a result of heat
treatment at 653 K for 6 h of *GaTe–CdTe* composite the low energy donor levels
are formed in *CdTe* crystallites. The temperature and excitation intensity depen-
dences for PL band in the region of 1.2 eV are analized in the work of Vatavu and
Gasin [58]. It can be concluded that the PL is determined by donor–acceptor
recombination with the participation of acceptor level of 9 meV. So we can admit
that interstitial oxygen in *GaTe* plates contribute to the formation of donor levels in
CdTe crystallites from composite. These levels form donor–acceptor complexes
responsible for PL in the range of 1.4–1.2 eV.

The composite consisting of *CdTe* and *GaTe* microcrystals was obtained by heat
treatment at temperatures from 623 to 833 K of *GaTe* single crystalline blades in *Cd*
vapor. The edge of absorption band of the composite that was obtained at the
temperature of 653 K is determined by direct optical transitions with the bandgap
width equal to 1.56 eV.

The PL spectra at the temperature of 78 K of *GaTe–CdTe* microcrystalline
composite obtained at the temperatures of 623–833 K is composed of PL bands of
both *CdTe* and *GaTe* crystallites. The PL spectra of studied samples are strongly
influenced by sample's temperature and are practical quenched at $T \geq 200$ K.
The PL intensity dependence on temperature is described by a formula of type (3) in
the temperature range of 78–200 K. As shown in Fig. 13.26 PL thermal activation
energy of PL band with maximum at 1.4 eV is 0.14 eV.

The own structural defects and uncontrollable impurities form in the intrinsic
band of *GaTe* semiconductor deep acceptor energy levels. Two acceptor levels with
the energies of 0.13 and 0.396 eV are formed in the intrinsic bandgap by interca-
lation of *Cd* into *GaTe*. The nonequilibrium charge carriers from CB recombine
with holes from the acceptor level with energy 0.13 eV in the temperature range of
80–140 K. The PL extinction process is determined by the acceptor level with
energy of 0.396 eV in the temperature range of 80–90 K. The process of photo-
luminescence extinction is dictated by the level with the energy of 0.396 eV.

13.5 Photoluminescence of Nanocomposites with *InSe* Lamellar Semiconductors

13.5.1 *InSe*

The PL spectrum at $T = 80$ K of n–*InSe* crystals is composed of at least two bands with peaks at 1.328 eV (A) and 1.314 eV (B) (Fig. 13.27). The edge band (A) is located in the spectral region of excitons in the state n = 1 (Fig. 13.28) and it can be considered as radiative annihilation of free exciton. The B band prevails in the spectrum. This band is shifted towards lower energies against to direct exciton emission band by 14 meV. The value is equal to the energy of optical phonons (A_{1g} vibration mode) in *InSe* semiconductor with rhombohedral lattice as shown in Fig. 13.27. The good correlation between the energy of optical phonon that are active in the formation of the edge of fundamental absorption band and the energy width between PL bands A and B (Fig. 13.27) indicates that B band is obtained as a result of excitons radiative annihilation with phonons emission of 14 meV. The electrical conductivity of *InSe* semiconductor is dominated by a donor center of small energy located at 23 meV from CB [59].

The stoichiometric *InSe* is a semiconductor with electrical conductivity through electrons. The changing of the type of majority charge carriers occurs as result of doping with small amounts of *Cd* and *Zn* [60, 61]. The doping of *InSe* with *Cd* in

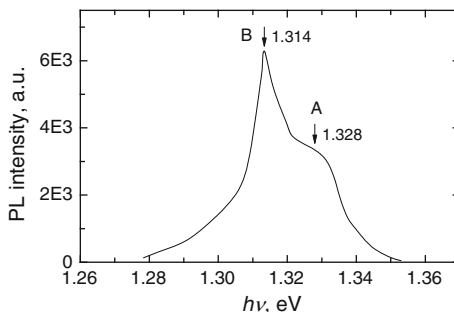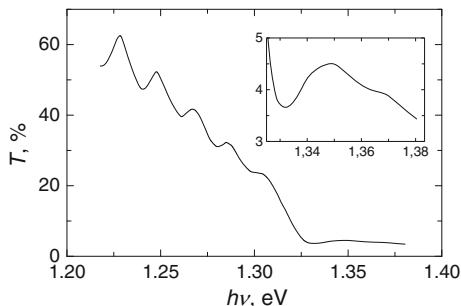Fig. 13.27 The PL spectrum of n-*InSe* crystals at $T = 80$ K

Fig. 13.28 The transmission spectrum in fundamental band edge region of a *InSe* with thickness of 11.2 μm at $T = 80$ K

concentration of 0.1–1.0 at.% changes the diagram of energy levels within bandgap by the formation of a deep acceptor level at 0.45 eV from VB [61]. Also, the *Cd* impurities form levels for holes with energies 0.42 and 0.48 eV from VB [62]. *Cd* in an amount of 0.1–1.0 at.% formes in the *InSe* band gap acceptor electronic states through which nonequilibrium charge carriers' radiative recombination occurs [63]. These recombination energy levels manifest themselves as electronic states of spatial defects induced in *InSe* lamella by splitting of single crystalline blocks [19].

13.5.2 InSe *Intercalated with* Cd

The PL spectra at $T = 80$ K of *InSe* crystals doped with 0.5 at.% *Cd* (a) and 1.0 at.% *Cd* (b) are presented in Fig. 13.29. The *Cd* with the concentration of C ≥ 0.5 at.% forms structural defects in the crystal lattice. This defects shield the excitonic bonds. The PL band caused by luminescencent annihilation of unionized excitons present in the spectrum of undoped *InSe* at 1.328 eV as well as its phonon replica is missing in PL spectra at $T ≥ 80$ K. However, the *Cd* impurity atoms form in a new band PL spectra at 1.17–1.27 eV. The maximum of impurity band in PL spectra of *InSe* crystals doped with 0.5 at.% *Cd* is found at energy of 1.215 eV. Since the width of bandgap for *InSe* cat $T = 80$ K is equal to 1.345 eV, the energy of acceptor level formed by *Cd* is equal to 0.13 eV from VB.

As shown in Fig. 13.29a on the wing of PL band at small energies it is present a band with maximum at 1.185 eV. This particularity of PL spectrum is formed as a result of luminescent transitions of nonequilibrium charge carriers from the acceptor level with energy of 0.16 eV. Note that the acceptor level with energy of 0.17 eV from VB were determined in the work of Shigetomi [63] by analyzing the temperature dependence of PL of the *InSe* doped with 5.0 at.% *Cd*.

The increasing of the *Cd* concentration from 0.5 to 1.0 at.% amplifies the band B, which maximum corresponds to photon energy of 1.20 eV. The maximum of band formed by *Cd* impurities at a concentration of 5.0 at.% is shifted to high
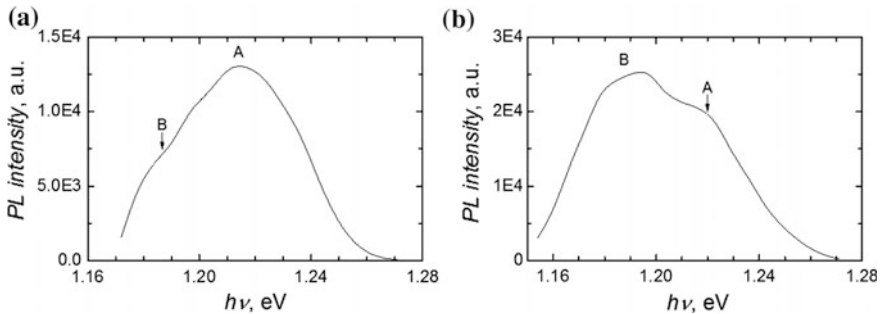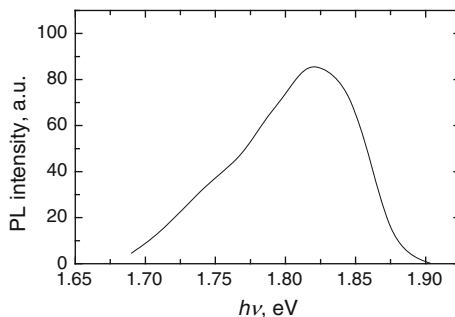

Fig. 13.29 The PL spectra at $T = 80$ K of *InSe* crystals doped with 0.5 at.% *Cd* (**a**) and 1.0 at.% *Cd* (**b**)

Fig. 13.30 The PL spectrum at $T = 293$ K of *InSe–Cd*Se micro-crystalline compound obtained by heat treatment at 773 K of *InSe* plates in *Cd* vapor for 3 h

energies by 10 meV in the work of Shigetomi [63]. Thus, we can consider those *Cd* impurity atoms with a concentration up to 1.0 at.% forme in the bandgap of *InSe* two acceptor levels at energies of 0.145 and 0.125 eV from VB.

The PL spectrum at $T = 293$ K of *InSe–CdSe* microcrystalline composite obtained by heat treatment in *Cd* vapor at 773 K of *InSe* plate for 3 h is shown in Fig. 13.30. The PL band with maximum at 1.83 eV is located at higher energies than the width of bandgap of crystalline compound from composite at $T = 293$ K: 1.30 eV for *InSe* [64] and 1.80 eV for *CdSe* [36]. The wing from lower energies of PL spectrum is localized in the energy range $hv \leq 1.80$ eV is formed by radiative recombination of nonequilibrium charge carriers in *CdSe* crystallites from composite. It is well known that the PL spectrum of *CdSe* compound in submicrometric particles represents a Gaussian band with maximum intensity in the wavelength region of 480–620 nm [43, 65, 66]. Thus, we can consider that anti–Stokes PL is determined by the presence of nanometrical *CdSe* crystallites in the composite.

13.5.3   InSe *Intercalated with* Zn

Zinc is one of the chemical elements that is used for doping of p–*InSe* compound [67]. The demand of study of the energy levels diagram formed by this dopant is determined by p–*InSe* perspective usage as photosensitive element in solar cells with high-energy efficiency [68]. The *Zn* forms acceptor levels at 0.16, 0.28, 0.31 eV and the capture level at 0.59 eV from the valence band within the bandgap of *InSe* compound. The energy level at 0.16 eV was determined from the analysis of temperature dependence of the PL impurity band using configurational coordinates model [69]. The levels with energies of 0.28, 0.31 and 0.59 eV were determined from measurements of the Hall effect [60, 70]. The presence of a emission band in the energy range of 1.05–1.28 eV with maximum at 1.17 eV determined by donor–acceptor recombination with *Zn* acceptor level at the energy of 0.13 eV it is characteristic for PL spectra of *InSe* crystals doped with *Zn* [71].

The PL spectrum at $T = 80$ K of *InSe–ZnSe* composite obtained by heat treatment of *InSe* plates in *Zn* vapor at 783 K for 21 h is shown in Fig. 13.31. The PL

Fig. 13.31 The PL spectrum at $T = 80$ K of *InSe–ZnSe* composite obtained by heat treatment at 783 K of *InSe* plates in *Zn* vapor for 21 h
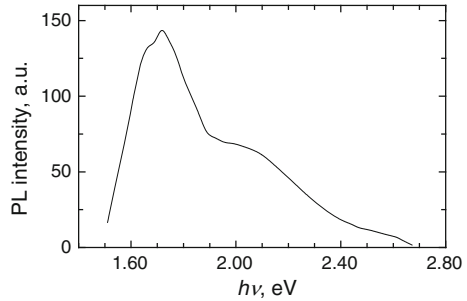
spectrum is composed of at least three wide bands with maxima respectively at 1.71, 2.10 and 2.58 eV. The width of bandgap of *InSe* compound at $T = 80$ K is equal to 1.342 eV. This value is much smaller than the energy of bands from the spectrum. So, the bands from the PL spectrum (Fig. 13.31) are determined by the processes of luminescent recombination in *ZnSe* crystallites from composite.

The PL spectrum of undoped *ZnSe* crystals at $T = 80$ K contains a band with maximum at 2.76 eV with symmetrical shape and FWHM of ∼55 meV. It is considered that this PL band has an excitonic nature [72]. The doping of *ZnSe* crystal with metals from I group (*Cu*, *Ag*, *Au*) leads to the formation of the large number of acceptor levels through which the PL bands are formed in the energy range from 450 to 1000 nm [73].

The temperature dependence of intensity of donor–acceptor recombination bands can be described by the expression (13.3). As shown in Fig. 13.32, the PL thermal quenching in the temperature range of 110–290 K of the band with maximum at energy 1.71 eV is well described by formula (13.3) for thermal activation energy equal to 0.045 eV.

The valence bonds at the edge of *InSe* plates are open, which imposes a much stronger interaction of *Zn* atoms from atmosphere surrounding plates with atoms from…–*Se–In–In–Se*–… packages. The PL spectra at respectively $T = 293$ K (a) and 80 K (b) from…–*Se–In–In–Se*–… planar packages interface are shown in Fig. 13.33a, b.

The PL spectrum of *ZnSe* crystallites from composite at room temperature is composed of two bands: the edge band with maximum at the energy of 2.460 eV and the broadband with maximum at 2.08 eV. The width of bandgap of *ZnSe* crystallite at $T = 293$ and 80 K is equal respectively to 2.680 and 2.793 eV [36]. At the intercalation temperature of 773 K the *Zn* atoms form the stable chemical compounds of *ZnSe* freeing the In atoms that serve as a dopant for both *InSe* and *ZnSe* crystallites from composite. The band from yellow–red spectral region is composed of two subbands with maxima at energies respectively of 2.08 and 1.72 eV. Thus, we can admit that In introduced in *ZnSe* crystallites forms at least three donor levels in his bandgap.

The three bands structure of PL spectrum of *ZnSe* crystallites from *ZnSe–InSe* composite is amplified when the compound is cooled down from 293 to 80 K
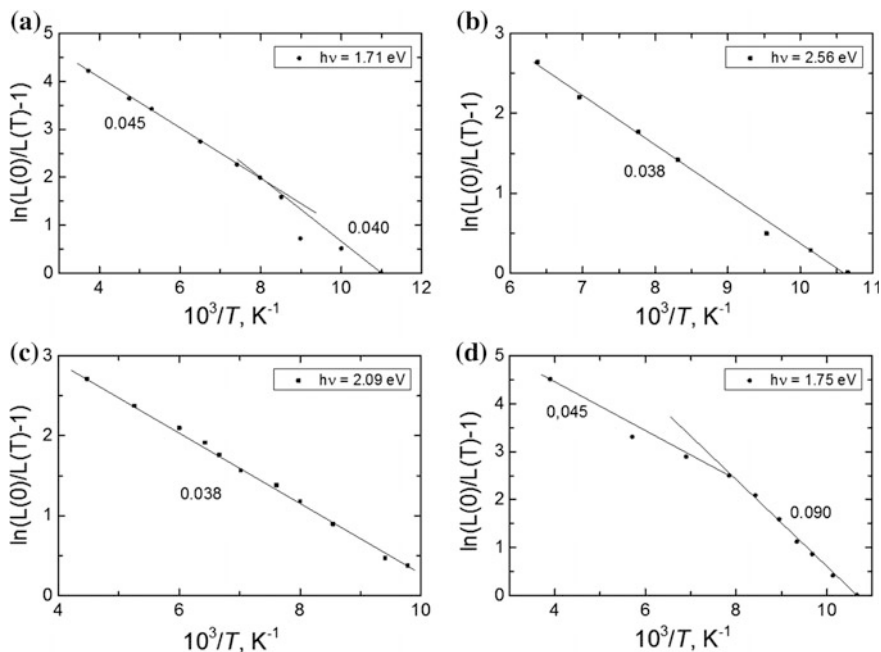
Fig. 13.32 The dependence of the PL peak intensity on the reciprocal temperature for 1.71 eV band from (0 0 0 1) surface of *InSe* plate (**a**) and bands from composite obtained on the *InSe* plate lateral side, with maxima at energies of 2.56 eV (**b**), 2.09 eV (**c**) and 1.75 eV (**d**)
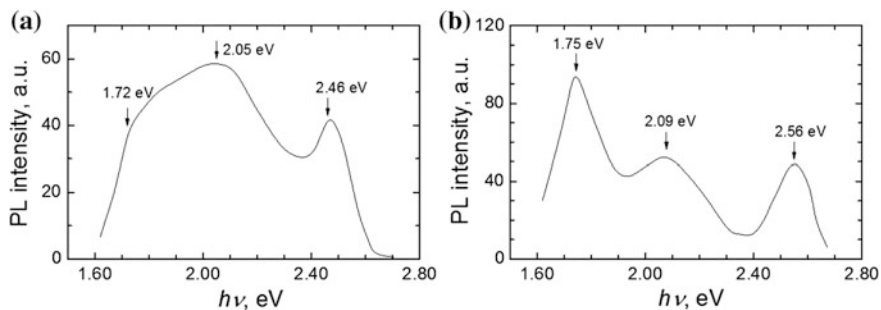

Fig. 13.33 The PL spectra from the lateral side of *InSe* plates that was heat treated at 783 K in *Zn* vapor for 21 h at: $T = 293$ K (**a**) and 80 K (**b**)

(Fig. 13.33). Three bands are present with maximum at energies of 2.560, 2.090 and 1.750 eV at this temperature. The coefficient of thermal shift of the edge band is equal to $\sim 5 \times 10^{-4}$ eV K^{-1}. This value is in good correlation with thermal shift of bandgap for this compound. The shifting to the lower energies of the bands from the red region of spectrum (2.09 and 1.75 eV) with thermal coefficients much lower

than the shift rate of the width of bandgap of *ZnSe* crystal occurs when the sample's temperature decreases.

At the sample's temperature decrease from 293 to 80 K, the PL bands intensity is reduced more than 60 times. As can be observed from Fig. 13.32, the temperature dependence of the PL intensity of the band with maximum at 1.71 eV (from the (0 0 0 1) surface of *InSe* plate) (Fig. 13.32a) and of those three PL bands of the composite formed on the edge of *InSe* plate with maximum at energies of 2.56 eV (Fig. 13.32b), 2.09 eV (Fig. 13.32c) and 1.75 eV (Fig. 13.32d) are well described by formula (13.3) for PL thermal activation energies of respectively 52, 45 and 38 meV. The PL band from the red region of the spectrum (peak at 1.75 eV), as shown in Fig. 13.32d can be characterized by two thermal activation energies: 90 meV at temperature range of 80–120 K and 45 meV in the temperature range of 120–290 K.

13.6 Conclusions and Generalities

- The *GaS* compound is an n-type semiconductor with indirect bandgap equal to 2.595 eV at $T = 78$ K. The phonons with average energy of 14 meV participate at the formation of the edge of indirect absorption band.
- The PL emission spectra of *GaS* lamella at $T = 78$ K contain a low intensity band close to the edge of indirect absorption band and a band with a slowly asymmetrical contour of donor-acceptor type with the maximum at the energy of 2.32 eV. The doping of *GaSe* crystals with 1 mol% of *Mn* attenuates the band with maximum at the energy of 2.32 eV and forms the characteristic band of *Mn* ions with the maximum at 1.92 eV in *GaS* and *GaSe* lamellar crystals. The PL band with maximum at the energy of 1.92 eV is obtained by the superposition of three Gaussian bands with peaks at 2.040, 1.972 and 1870 eV. The donor-acceptor nature of these bands is proved by the dependence of the PL intensity from the temperature.
- The material composed of *GaS* and *ZnS* nanocrystallites that are photoluminescent in the purple-orange region of the spectrum was obtained by the heat treatment at the temperature of 753 K of *GaS* single crystals in *Zn* vapour. The PL spectrum of *GaS–ZnS* nanocomposite is formed by overlapping of *GaS* and *ZnS* crystallites individual bands.
- The PL spectrum of *GaSe* single crystals at $T = 78$ K is composed of emission bands of localized excitons and their phonon repetitions and the donor-acceptor band with maximum at energy 1.91 eV. The PL spectrum of *GaSe–CdSe* nanocomposite can be presented as band composed of four sub-bands that have the Gauss contour. The PL sub-bands are interpreted as the PL emission of CdSe microcrystallites and nanocrystallites that sizes are from units to tens of nanometers.
- The structure of PL spectrum of *GaTe–CdTe* nanocomposite obtained by heat treatment at 653–833 K was studied. The *GaTe* plates kept for a long time in

normal atmosphere were used as basic material. It was established that the PL activation energy depends weak on the treatment temperature of *GaTe* plates in *Cd* vapour.

- *InSe−ZnSe* and *InSe–CdSe* nanocomposites are materials that are photoluminescent in the red-NIR region of the spectrum. The presence of antistokes luminescence is determined by the nanometric dimensions of the *ZnSe*, *CdSe* and *InSe* crystallites which serve as components of studied composite materials.

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