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Analysis of luminescence method applicability for determination of $Cd_{1-x}Zn_xTe$ composition

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Abstract. Physical fundamentals are analyzed for the method of determination of $Cd_{1-x}Zn_xTe$ composition x from measurements of the luminescence band peak position, emission being caused by annihilation of bound exciton – shallow neutral acceptor complexes at 4.2 K. Found are the conditions when application of the method discussed enables to obtain reliable x values.

Keywords: $Cd_{1-x}Zn_xTe$ composition, excitons, exciton-impurity complexes, luminescence.

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1. Introduction and problem formulation

The use of luminescence method (measurement of the luminescence band peak position $h\nu_m$) is very convenient way for determination of the chemical composition of ternary II-VI compound semiconductors $Cd_{1-x}Zn_xTe$. That is why, the aim of many works was to obtain the dependencies of the peak position of different luminescence bands in $Cd_{1-x}Zn_xTe$ as a function of their composition x, which could enable to find x values from the $h\nu_m$ measurements. So, in [1–3] this dependence was found at $T = 4.2$ K for the luminescence band caused by annihilation of excitons X bound with shallow neutral acceptors A^0 (i.e. by exciton - impurity complexes A^0X). The discussed dependence $h\nu_m(x)$ (the emission is induced by annihilation of excitons) was determined at $T = 12$ [4] and 77 K [5], too. But in these works the type of excitons that give rise to the investigated emission was not determined. Besides that, the 300 K $h\nu_m(x)$ dependence for the intrinsic luminescence band is known [4]. Naturally, in principle, the 300 K $h\nu_m$ vs. x changes for band-to-band recombination could also be found from the registered dependencies of the $Cd_{1-x}Zn_xTe$ bandgap E_g on x at $T = 300$ K (see [6–9]) [$h\nu_m = E_g + (1/2)kT$ for the intrinsic emission band at room temperature (k is the Boltzmann constant and T is the absolute temperature), see Appendix 1]. But contrary to the expected, it does not correlate with $h\nu_m$ known for band-to-band transitions at 300 K against zinc concentration variations for $Cd_{1-x}Zn_xTe$ ternary alloys (see Appendix 2). Obviously, determination of $Cd_{1-x}Zn_xTe$ composition from the peak position of the intrinsic emission band is also possible at low temperatures ($T = 4.2$ K) as the dependence of the energy gap for the pointed compound on x for the above-mentioned temperature is known [1,7,8,10,11] ($h\nu_m = E_g$ for band-to-band transitions at liquid helium temperature, see Appendix 1). In principle, the x-value could also be found from the compositional variations of the 2 K peak position of the free exciton-induced emission band [10].

But usage of the known 12 and 77 K dependencies of the peak position of exciton emission bands at different x for determination of $Cd_{1-x}Zn_xTe$ composition is not sufficiently reliable, as in [4,5] the exciton type that induces the studied emission was not established. Besides that, evidently, the $h\nu_m$ measurement at $T = 12$ K is inconvenient, and the $h\nu_m(x)$ dependence at $T = 77$ K was obtained only in a narrow region of x – values ($0 \le x \le 0.2$). Obviously, rather complex are measurements of the 2 K free exciton-induced emission intensities. Also, problems exist when one uses the measurement of 300 and 4.2 K peak positions of the intrinsic emission band to find the x values. Firstly, 300 K shape of the near-band-edge spectrum is only partially caused by band-to-band recombination, with some contribution from the free exciton transitions and their phonon replicas [12]. So, it is rather difficult to separate the intrinsic emission band from the near-band-edge luminescence spectrum; the latter substantially lowers the accuracy of determination of $Cd_{1-x}Zn_xTe$ composition from the peak position of the intrinsic luminescence band at 300 K [12,13] (see Appendix 2). Secondly, the

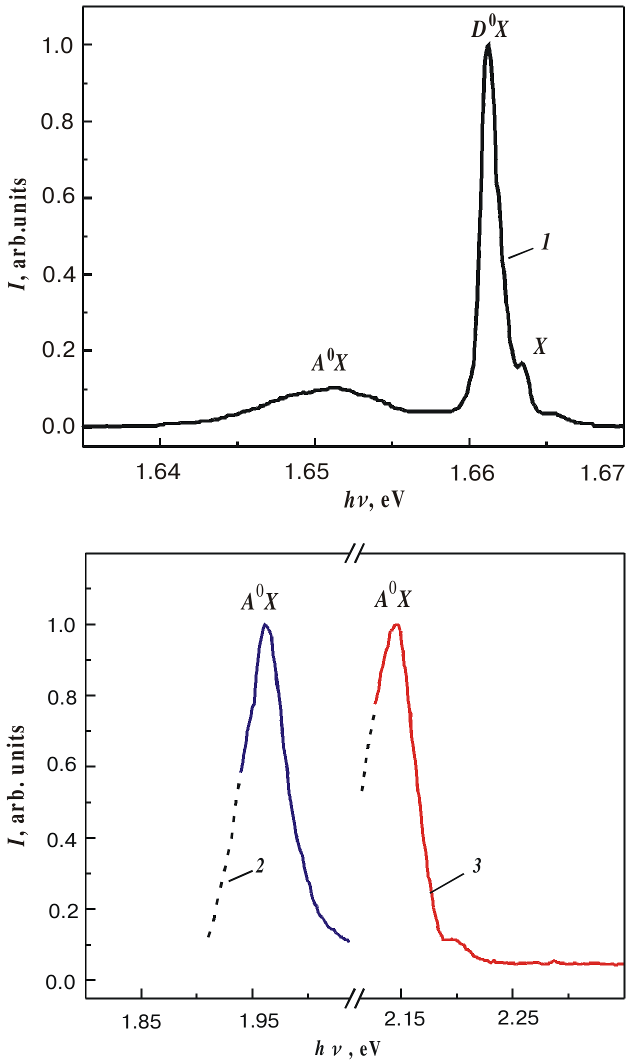

Fig. 1. Typical 4.2 K excitonic luminescence spectra of $Cd_{1-x}Zn_xTe$ with $x = 0.1$ (*1*), 0.54 (*2*) and 0.84 (*3*). $h\nu_m$ (A^0X) = 1.652 (*1*), 1.908 (*2*) and 2.202 eV (*3*).

intensity of the 4.2 K intrinsic emission is rather low due to existence of effective channels for non-radiative recombination of excess electrons and holes in $Cd_{1-x}Zn_xTe$ (effectively, the intrinsic luminescence band is absent in the 4.2 K near-band-edge spectrum of $Cd_{1-x}Zn_xTe$, see, for example [13–18]).

Therefore, the measurements of 4.2 K peak position of the luminescence band arising due to annihilation of exciton-impurity complexes A^0X (Fig. 1) are so widely spread in determining $Cd_{1-x}Zn_xTe$ chemical composition (see, for example [19–21]) {some attention was paid to determining $Cd_{1-x}Zn_xTe$ compositional uniformity by mapping the room-temperature peak position of the intrinsic emission band (see, for example, [13,22,23] and references therein)}. The corresponding $h\nu_m(A^0X)$ vs. x calibration dependencies at $T = 4.2$ K [the 4.2 K compositional dependencies of $h\nu_m(A^0X)$] are analytically described by the following expressions:

$$h\nu_m = (1.590 + 0.322x + 0.463x^2)\ \text{eV} \tag{1}$$

for $Cd_{1-x}Zn_xTe$ films {see Fig. 2 and Appendix 3.1 about the accuracy of the x-measurement using Eq. (1)} [1], and

$$h\nu_m = (1.590 + 0.445x + 0.339x^2)\ \text{eV} \tag{2}$$

for $Cd_{1-x}Zn_xTe$ crystals [see Fig. 3 and Appendix 3.2 about the form of the calibration dependence (2) and the accuracy of the x-measurements using Eq. (2)] [2,3]. But,

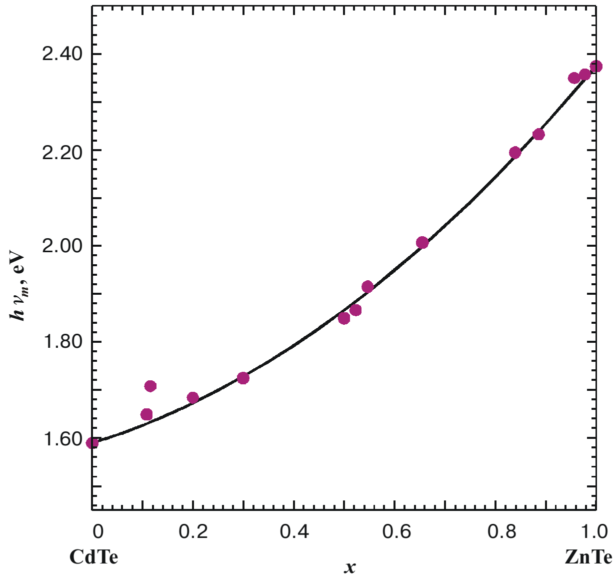

Fig. 2. Dependence of the peak position of the luminescence band, induced by annihilation of bound excitons A^0X in $Cd_{1-x}Zn_xTe$ films as a function of their composition x at $T = 4.2$ K. The solid line is constructed accordingly to Eq. (1). For convenience experimental $h\nu_m$ vs. x points are also shown (see the text).

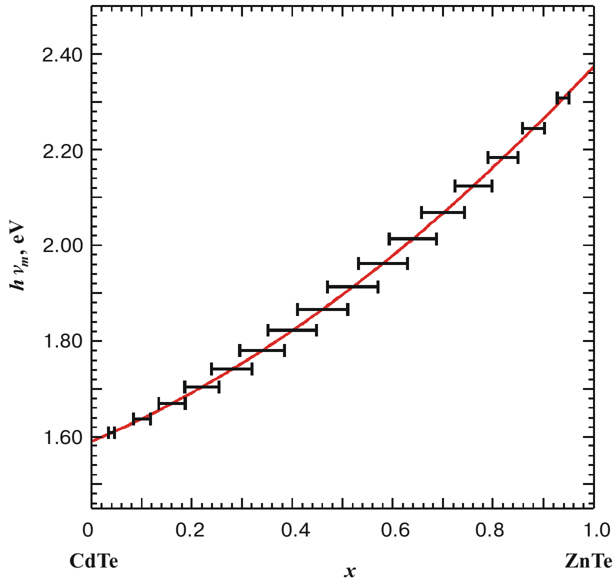

Fig. 3. Dependence of the peak position of the luminescence band, induced by annihilation of bound excitons A^0X in $Cd_{1-x}Zn_xTe$ crystals as a function of their composition x at $T = 4.2$ K. The curve is drawn accordingly to the relation (2).

when finding the cadmium zinc telluride composition, insufficient attention was paid to the correctness of the x – determination by the considered luminescence method. The pointed refers to the following.

In the low-temperature ($T = 4.2$ K) excitonic luminescence spectrum of $Cd_{1-x}Zn_xTe$, one could observe not only the examined emission band [its peak position $h\nu_m(A^0X) = 1.590$ eV at $x = 0$ and 2.375 eV at $x = 1$], but also other emission bands (Fig. 1) [13–18]. One of them is caused by annihilation of excitons bound with shallow neutral donors D^0 [i.e. by exciton-impurity complexes D^0X, the peak position of the corresponding emission band $h\nu_m(D^0X) = 1.594$ eV at $x = 0$ and 2.3785 eV at $x = 1$] (see, for example [13–18] and Fig. 1). Another one arises from recombination of free excitons X [the emission band peak position $h\nu_m(X) = 1.596$ eV at $x = 0$ and 2.381 eV at $x = 1$] (see, for example [13–18] and Fig. 1). Evidently, the simple identification of the emission band with $h\nu_m = h\nu_m(A^0X)$ is possible if in the excitonic luminescence spectrum the emission bands caused by annihilation of bound (A^0X, D^0X) and free (X) excitons are observed as for them $h\nu_m(A^0X) < h\nu_m(D^0X) < h\nu_m(X)$ (see Fig. 1, Table 1 and references [13–20,24]). But if in the spectrum not all pointed excitonic emission bands are observed, then the identificationof the emission band induced by annihilation of bound excitons A^0X at $x > 0$ in it meets some difficulties. Really, if the excitonic luminescence spectrum consists of two emission bands, then, obviously, the identification of A^0X luminescence band is possible only if besides the dependence $h\nu_m(A^0X) = \varphi(x)$ other dependencies such as $h\nu_m(D^0X) = \varphi(x)$ or $h\nu_m(X) = \varphi(x)$ are known. But in the literature dependencies $h\nu_m(D^0X)$ and $h\nu_m(X)$ as functions of x are absent (only fragmentary data of some authors about $h\nu_m(D^0X)$ and $h\nu_m(X)$ at several x-values exist, see Table 1 and Fig. 4). If the excitonic emission spectrum consists only of the single luminescence band (see, for example [19, 21, 23] and Fig. 1), then the identification of the emission band induced by annihilation of bound excitons A^0X obviously is not possible, even if the dependencies $h\nu_m(A^0X)$, $h\nu_m(D^0X)$ and $h\nu_m(X)$ vs. x are known. Undoubtedly, this fact essentially complicates application of the luminescence method for determination of $Cd_{1-x}Zn_xTe$ composition.

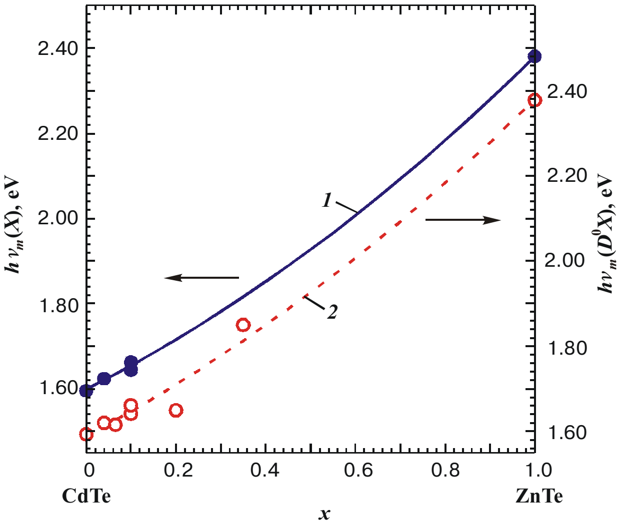

Fig. 4. Plots of the 4.2 K peak positions of luminescence bands, induced by annihilation of free X (1) and bound D^0X (2) excitons in $Cd_{1-x}Zn_xTe$ versus Zn concentration [$h\nu_m(X)$ and $h\nu_m(D^0X)$ values are taken from the Table 1].

In what follows, we will analyze the physical fundamentals of the x-determination in $Cd_{1-x}Zn_xTe$ by studying the low temperature ($T = 4.2$ K) peak position of the emission band induced by annihilation of bound exciton – shallow neutral acceptor complexes.

Table 1. Peak positions of luminescence lines induced by annihilation of bound(A^0X, D^0X) and free (X) excitons in $Cd_{1-x}Zn_xTe$ of different compositions at $T = 4.2$ K.

x	$h\nu_m(A^0X)$, eV	$h\nu_m(D^0X)$, eV	$h\nu_m(X)$, eV (n=1)	References
0	1.590	1.594	1.596	[25-28]
0.04	1.616	1.621	1.624	[15]
0.04	1.6167	1.6204	1.6247	[14]
0.065	1.616			[10]
0.1	1.632	1.642	1.644	[16]
0.1	1.652	1.662	1.6635	[13]
0.2		1.65		[23]
0.35		1.85		[23]
1	2.375			[1,2,27]
1	2.3692	2.3785	2.381	[14]

2. Analysis of the method

We will consider semiconductors at low ($T \le 4.2$ K) temperatures [no thermally stimulated processes are observed in them, their conductivity is determined by uniformly distributed photoelectrons (concentration δn) and photoholes (concentration δp)]. Let them contain shallow acceptors A (their concentration N_A, the hole and electron capture coefficients are c^-_{pA} and c^0_{nA}, accordingly), and shallow donors D (their concentration N_D, the hole and electron capture coefficients are c^0_{pD} and c^+_{nD}). A part of acceptors and donors could be in a neutral state (their concentrations N_{A^0} and N_{D^0}). A small number of neutral acceptors A^0 and neutral donors D^0 could bind free excitons (their concentration n_X, the probability of direct annihilation a_X), forming exciton-impurity complexes A^0X and D^0X (binding coefficients are b_{A^0X} and b_{D^0X}, binding probabilities $b_{A^0X}N_{A^0}$ and $b_{D^0X}N_{D^0}$). Evidently, for a discussed case intensities of the excitonic emission bands [induced by annihilation of bound excitons $A^0X(I_{A^0X})$, $D^0X(I_{D^0X})$ and free excitons $X(I_X)$] will be given by the following relations {when writing Eqs (3) and (4), we assumed that the exciton annihilation proceeds mainly with the photon emission [25,26]}:

$$I_{A^0X} = b_{A^0X} N_{A^0} n_X\,, \quad I_{D^0X} = b_{D^0X} N_{D^0} n_X\,, \tag{3}$$

$$I_X = \alpha_X n_X\,, \tag{4}$$

where

$$\begin{aligned} N_{A^0} &= \frac{c^-_{pA}\delta p}{c^-_{pA}\delta p + c^0_{nA}\delta n} N_A\,, \\ N_{D^0} &= \frac{c^+_{nD}\delta n}{c^+_{nD}\delta n + c^0_{pD}\delta p} N_D\,, \end{aligned} \tag{5}$$

$$n_X = \frac{b_X \delta p \delta n}{\alpha_X + b_{A^0X} N_{A^0} + b_{D^0X} N_{D^0}} \tag{6}$$

[here b_X is the binding coefficient of a hole-electron pair into a free exciton; the relations (5) and (6) are valid at $L > 0$].

As one could see from Eqs (3) and (4), the relation between intensities of the excitonic emission bands could be presented in the following form:

$$I_{A^0X} : I_{D^0X} : I_X = b_{A^0X} N_{A^0} : b_{D^0X} N_{D^0} : \alpha_X \tag{7}$$

When analyzing Eq. (7) one must take into account the following things: 1) The b_{A^0X} and b_{D^0X} values are nearly equal, i.e. $b_{A^0X} \approx b_{D^0X}$ at any x, as was found from the theoretical relation $b_{A^0X}/b_{D^0X} = (I_{A^0X}/I_{D^0X}) N_{D^0}/N_{A^0}$ [see Eq. (3)] using the experimental I_{A^0X}/I_{D^0X}, N_{D^0} and N_{A^0} values ($N_{D^0} \approx N_D$ and $N_{A^0} \approx N_A$, see below). 2) In compound semiconductors (as in elementary ones [25]) the inequalities $c^-_{pA}\delta p >> c^0_{nA}\delta n$ and $c^+_{nD}\delta n >> c^0_{pD}\delta p$ are fulfilled; then, as follows from Eq. (5), $N_{A^0} \approx N_A$ and $N_{D^0} \approx N_D$. In this case [see Eq. (7)], the emission band induced by annihilation of bound excitons A^0X dominates in the excitonic luminescence spectrum ($I_{A^0X} >> I_{D^0X}, I_X$), if, firstly, $N_A >> N_D$ (then $b_{A^0X}N_{A^0} >> b_{D^0X}N_{D^0}$), and , secondly, the free excitons disappear mainly due to their binding by shallow acceptors [then $b_{A^0X}N_{A^0} + b_{D^0X}N_{D^0} \approx b_{A^0X}N_{A^0} >> \alpha_X$, and, consequently, $n_X \cong b_X \delta p \delta n / b_{A^0X}N_{A^0}$, see Eq. (6); this is confirmed by the fulfillment of the relation $I_X << I_{A^0X} + I_{D^0X} \approx I_{A^0X}$]. Evidently, the pointed inequality $N_A >> N_D$ could be fulfilled not only in a low resistivity p-type $Cd_{1-x}Zn_xTe$ (the specific resistivity $\rho \le 10^3$ Ohm·cm at $T = 300$ K, its dark conductivity is determined by ionization of shallow acceptors), but in a high resistivity p- and n-type cadmium zinc telluride too ($\rho \cong 10^4$–10^{10} Ohm·cm at $T = 300$ K), if its dark conductivity is determined by ionization of partly compensated deep donors (then their concentration $N^*_D > N_A - N_D > 0$) [undoubtedly, if the dark conductivity of $Cd_{1-x}Zn_xTe$ is determined by ionization of partly compensated deep acceptors (it is possible, if their concentration $N^*_A > N_D - N_A > 0$), then in this case the concentration of shallow acceptors is less then the concentration of shallow donors]. Evidently, for a discussed case in the excitonic luminescence spectrum (independently of the number of emission bands in it) the luminescence band induced by annihilation of bound excitons A^0X dominates. The intensity of the A^0X emission band is equal to a generation rate of free excitons $b_X\delta p\delta n$($I_{A^0X} \cong b_X\delta p\delta n$), as in a discussed case the latter are mainly transformed into bound exciton-shallow neutral acceptor complexes A^0X.

3. Conclusions

Therefore, application of the luminescence method for determination of $Cd_{1-x}Zn_xTe$ chemical composition (from the measurements of the $T = 4.2$ K peak position of the emission band caused by annihilation of bound excitons A^0X) is possible in two cases. The first one – in an excitonic part of $Cd_{1-x}Zn_xTe$ luminescence spectrum the emission bands induced by annihilation of bound A^0X, D^0X and free excitons X are observed. Then, obviously in $Cd_{1-x}Zn_xTe$ of any type (p-, n-) and value of dark conductivity, one can clearly identify the luminescence band induced by annihilation of bound excitons A^0X. The second one – if in a ternary compound $Cd_{1-x}Zn_xTe$, at first, the relation $N_A >> N_D$ is fulfilled (low resistivity p-type $Cd_{1-x}Zn_xTe$ and high resistivity p- or n- type $Cd_{1-x}Zn_xTe$

with partly compensated deep donors), and, secondly, radiative annihilation of free excitons is an ineffective (as compared with the processes of their binding by shallow acceptors and donors) channel of their disappearance. Then, in the excitonic part of $Cd_{1-x}Zn_xTe$ luminescence spectrum at 4.2 K, an intense A^0X emission band is observed.

Appendix

1. *Peak position $h\nu_m$ and half-width w of the intrinsic emission band*

Let us consider non-degenerated weakly excited direct-gap semiconductors (in them the kinetic energy of most electrons and holes $\varepsilon \le kT$). In this case, the peak position of the intrinsic emission band $h\nu_m$ and its half-width w are given by the following relations (evidently, the majority of recombining electrons and holes emit photons with the energy $h\nu \le E_g + kT$, i.e. $h\nu - E_g \le kT$):

$$h\nu_m = E_g, \qquad w = 0.7\,kT, \tag{A1}$$

if the Coulombic interaction between electrons and holes is strong enough, i.e. the free exciton binding energy ε_B ($\varepsilon_B \approx 10$ meV for CdTe and ZnTe [2, 10, 23, 27]), exceeds substantially the average kinetic energy of electrons and holes ($\varepsilon_B >> kT$, then, evidently, $\varepsilon_B >> h\nu - E_g$ in the actual region of the intrinsic emission) {see Eq. (1.14) in [29]}, and

$$h\nu_m = E_g + \frac{1}{2}kT, \qquad w = 1.8\,kT, \tag{A2}$$

if interaction between electrons and holes is practically absent, i.e. the exciton binding energy is much smaller than the average kinetic energy of recombining electrons and holes ($\varepsilon_B << kT$, then, obviously, $\varepsilon_B << h\nu - E_g$ in tne actual region of the intrinsic emission) {see Eq.(1.14) in [29] and also references [12, 30]}.

Therefore, contrary to the stated in [29], Eq. (A1) should be used only at low temperatures ($kT << \varepsilon_B$, then a strong interaction of electron-hole pairs exists), and Eq. (A2) is applicable at high temperatures ($kT >> \varepsilon_B$, then non-interacting electrons and holes are involved in recombination transitions).

2. *A comparison of experimental and theoretical (obtained from the energy gap E_g vs. x variations) compositional dependences of the intrinsic emission band peak position for $Cd_{1-x}Zn_xTe$ at 300 K*

The known variations of $Cd_{1-x}Zn_xTe$ band gap E_g at 300 K with composition are described by the following relations (pay attention to a significant difference in E_g vs. x dependencies given below, but there is no obvious basis for choosing one relation over another) [see Fig. 5]:

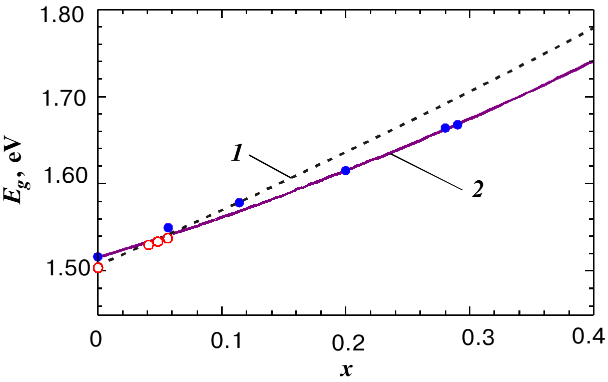

Fig. 5. Plots of the 300 K band gap E_g vs. x in $Cd_{1-x}Zn_xTe$. *1* – the data of [7] (see Eq. (A3)); *2* – the data of [9] (see Eq. (A4)). For convenience, experimental E_g vs. x points are also shown.

$$E_g = (1.5045 + 0.631x + 0.128x^2)\ \text{eV} \tag{A3}$$

according to [7],

$$E_g = (1.516 + 0.429x + 0.334x^2)\ \text{eV} \tag{A4}$$

according to [9] {note a wide spread in E_g values at $x = 0$ [$E_g = 1.5045$ eV, see Eq. (A3), $E_g = 1.516$ eV, see Eq. (A4)]; other E_g values at $x = 0$ (1.505 – 1.515 eV) could also be found in the literature [12]}.

So, one expects that the theoretical dependence of the peak position of the intrinsic emission band $h\nu_m$ for lightly doped weakly excited $Cd_{1-x}Zn_xTe$ at 300 K [evidently, $h\nu_m = E_g + (1/2)kT$, see Appendix 1] is given by the expression [see Eq. (A3) and Fig. 6] :

$$h\nu_m = (1.517 + 0.631x + 0.128x^2)\ \text{eV} \tag{A5}$$

or by the relation [see Eq. (A4) and Fig. 6]:

$$h\nu_m = (1.5285 + 0.429x + 0.334x^2)\ \text{eV}. \tag{A6}$$

Evidently, a presence of various 300 K $h\nu_m$ vs. x dependencies [see Eqs (A5), (A6) and Fig. 6] casts doubt on the use of Eqs (A5) and (A6) for determination of $Cd_{1-x}Zn_xTe$ composition with the acceptable accuracy.

However, in an experiment substantially different to the expected from Eqs (A5) and (A6) $h\nu_m$ vs. x dependence is observed – the opinion of the authors [4] is that variations in the 300 K peak position of the luminescence line induced by band-to-band transitions, as $Cd_{1-x}Zn_xTe$ composition is changed, are given by the following equation (see Fig. 6):

$$\begin{aligned} h\nu_m = {} & [(1.510 \pm 0.005) + (0.606 \pm 0.010)x + \\ & + (0.139 \pm 0.010)x^2]\ \text{eV} \end{aligned} \tag{A7}$$

{it was erroneously considered in [4] that $h\nu_m = E_g$ at 300 K [one expects that $h\nu_m = E_g + (1/2)kT$ at room temperature, see Appendix 1]}.

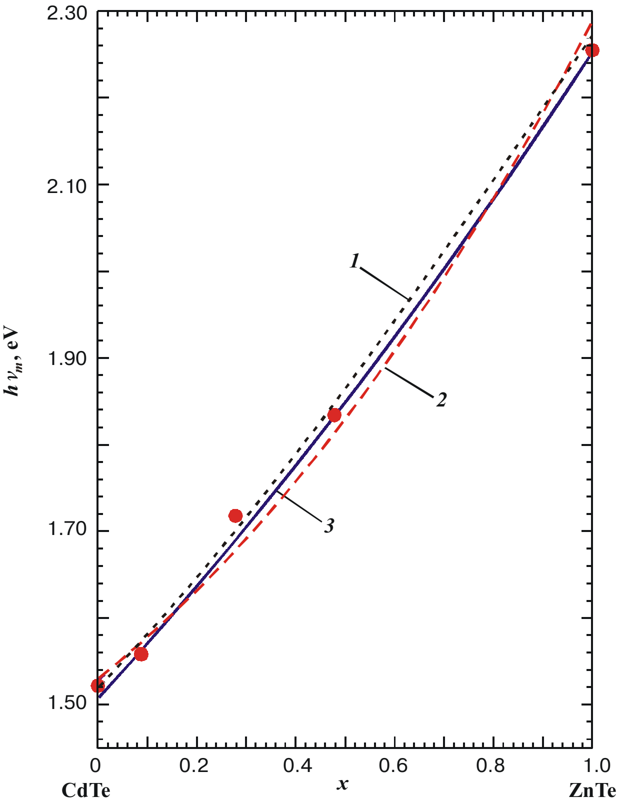

Fig. 6. Plots of the 300 K peak position of the luminescence band caused by band-to-band transitions of free electrons and holes $h\nu_m$ in $Cd_{1-x}Zn_xTe$ versus Zn concentration. The 300 K $h\nu_m$ vs. x dependencies are constructed accordingly to Eqs (A5) (*1*), (A6) (*2*) and (A7) (*3*). For convenience, experimental $h\nu_m$ vs. x points are also shown. The experimental $h\nu_m$ values are partially influenced by free exciton annihilation (see the text).

Reasons for an appearance of differing theoretical and experimental $h\nu_m$ vs. x dependencies [see Eqs (A5)–(A7) and Fig. 6] are not understood up to date. One of them may be as follows [it concerns $h\nu_m$ vs. x dependencies given by Eqs (A5) and (A7), for which experimental $h\nu_m$ values are smaller than the theoretical ones at any x, see Fig. 6, curves 1 and 3].

The authors of [4] considered that the near-band-edge luminescence band arises at 300 K due to band-to-band transitions of free electrons and holes. But it is now believed (see, for example [12, 13, 23]) that 300 K near-band-edge luminescence of $Cd_{1-x}Zn_xTe$ (as that of GaAs, see [30]), occurs not only due to free electron – free hole recombination, but also due to free exciton annihilation. The free exciton contribution is rather large, so the peak position of the near-band-edge luminescence band at 300 K shifts significantly to the low energy region (for example, to $h\nu_m$ = 1.50–1.504 eV at $x = 0$ [12,31]). Obviously, the discussed free exciton contribution into near-band-edge luminescence at 300 K should be taken into account, if one wants to construct the reliable 300 K $h\nu_m$ vs. x calibration dependencies for determining Zn content in $Cd_{1-x}Zn_xTe$.

3. Analysis of available $h\nu_m(A^0X)$ vs. x dependencies at 4.2 K

3.1. $Cd_{1-x}Zn_xTe$ films. The 4.2 K $h\nu_m(A^0X)$ vs. x calibration Eq. (1) for $Cd_{1-x}Zn_xTe$ films is the best quadratic fit to the data going through the known experimental points (see Fig. 2) [1]. But one can observe a rather substantial deflection of some experimental points from the calibration curve [it is at maximum at low x–values ($x \le 0.2$)] (see Fig. 2). It is scarcely probable that this difference is caused by the accuracy of $h\nu_m(A^0X)$ and x–measurements {usually the inaccuracy of the $h\nu_m(A^0X)$ measurement do not exceed ±0.5 meV and the x measurement ±1% [3]}. Besides that, the observed rather strong deflection of experimental and theoretical $h\nu_m$ points in the $h\nu_m$ vs. x dependence at low x values ($x \le 0.2$) cannot be connected with the possible $Cd_{1-x}Zn_xTe$ compositional non-uniformity Δx (usually $\Delta x/x$ = 0.03–0.15, see [13, 22, 23]), i.e. the latter gives only a small contribution to the discussed non-coincidence of $h\nu_m$ experimental and theoretical points, as in $Cd_{1-x}Zn_xTe$ films of low zinc concentrations ($0.463x << 0.322$, i.e. $x << 0.7$) an approximately linear relation between $h\nu_m$ and x holds – $h\nu_m \approx (1.590 + 0.322x)$ eV [see Eq.(1)] (evidently, if a strictly linear relation between $h\nu_m$ and x takes place, i.e. $h\nu_m = a + bx$, where $a, b \neq \varphi(x)$, then the semiconductor compositional non-uniformity brings no contribution into the discussed non-coincidence of $h\nu_m$ experimental and theoretical points). Undoubtedly, an essential contribution of $Cd_{1-x}Zn_xTe$ compositional non-uniformity into the deflection of $h\nu_m$ experimental and theoretical points in the $h\nu_m$ vs. x dependence is possible only at high x-values ($x \ge 0.3$, then $0.332 \approx 0.463x$) as in this case $h\nu_m$ depends non-linearly on x [see Eq. (1)].

Most probably, the discussed deflection of experimental and theoretical points in the $h\nu_m(A^0X)$ vs. x dependence is associated with some poorly controllable properties of $Cd_{1-x}Zn_xTe$ films, which influence the $h\nu_m(A^0X)$ value at a given x (for details, see subsection 3.2 below). Obviously, the pointed leads to a definite inaccuracy in obtained x-values by the examined luminescence method. This inaccuracy is of the order of ±20% for x = 0.03–0.1, ±5–10 % for $0.2 \ge x > 0.1$, 2 – 5% for $0.5 \ge x > 0.2$ and 1–2 % for $0.95 \ge x > 0.5$ as follows from the detailed examination of Fig. 2 (when calculating inaccuracies at low x-values, we did not take into account the experimental point $h\nu_m \cong 1.71$ eV at $x \approx 0.11$).

3.2. $Cd_{1-x}Zn_xTe$ crystals. In the literature, two essentially different $h\nu_m(A^0X)$ vs. x dependencies at T = 4.2 K for $Cd_{1-x}Zn_xTe$ mixed crystals could be found (there is no obvious basis for preferring one dependence over another). They are (note that a difference between them exceeds considerably the inaccuracies of the $h\nu_m$ and x measurements, see Fig. 7):

$$h\nu_m = (1.591 + 0.241x + 0.542x^2)\ \text{eV} \tag{A8}$$

according to [2] (see Fig. 7) [it is the best fit of experimental points], and

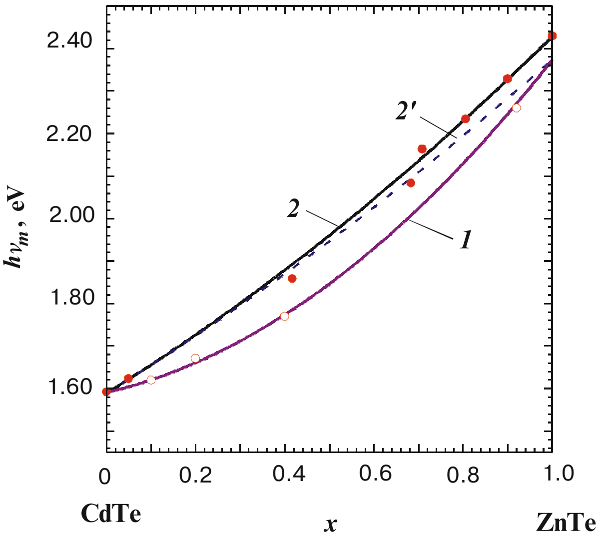

Fig. 7. Plots of the 4.2 K peak position of the luminescence band, induced by annihilation of bound excitons A^0X in $Cd_{1-x}Zn_xTe$ crystals against Zn concentration. (*1*) – the data of [2] (the solid line is calculated from Eq. (A8)); (*2*) – the data of [3] (the solid line is calculated from Eq. (A9)); (*2′*) – the corrected data of [3] [the dashed line is calculated from Eq. (A10)]. For convenience, experimental $h\nu_m$ vs. x points are also shown (see the text).

Table 1A. $Cd_{1-x}Zn_xTe$ chemical composition as determined by the X-ray microanalysis (x) and by the luminescence method [using Eq. (2)] (x*).

$h\nu_m(A^0X)$ at T = 4.2 K, eV	x	References	x*
1.616	0.04	[15]	0.056±0.009
1.6167	0.04	[14]	0.058±0.009
1.632	0.1	[16]	0.088±0.015
1.652	0.1	[13]	0.127±0.022
1.642	0.12		0.108±0.019
1.65	0.125		0.123±0.021

Note. The accuracy of x-measurements is not given in [13–16].

$$h\nu_m = [1.589 + (0.65 \pm 0.01)x + (0.19 \pm 0.02)x^2]\ \text{eV} \quad \text{(A9)}$$

according to [3] (see Fig. 7).

The equation (A9) gives the $h\nu_m(A^0X)$ value at x = 1 (2.429 eV) substantially exceeding the known one for ZnTe (2.375 eV), see, for example [1, 2, 14, 27]. So, a correction must be inserted into Eq. (A9). The corrected Eq. (A9) [it gives $h\nu_m(A^0X)$ = 2.375 eV at x = 1] is of the form (see Fig. 7):

$$h\nu_m = (1.589 + 0.65x + 0.136x^2)\ \text{eV}. \quad \text{(A10)}$$

The equation (2) given above shows the "averaged" [according to Eqs (A8) and (A10)] $h\nu_m(A^0X)$ vs. x dependence.

The pointed difference in the shapes of $h\nu_m(A^0X)$ vs. x dependencies [see Eqs (A8) and (A9)] is not connected with the possible different origin of dominating shallow acceptors in crystals studied in [2,3]. Really, the peak position of the A^0X emission band could only slightly differ (by ±1 meV) for shallow acceptors of different origin (see, for example [27, 28]). So, the discussed rather large difference of $h\nu_m(A^0X)$ values at fixed x essentially exceeds the expected one for the CdTe + ZnTe system, arising due to a different origin of shallow acceptors in it (see Fig. 7). Most probably, the observed difference in the shapes of $h\nu_m(A^0X)$ vs. x dependencies for different $Cd_{1-x}Zn_xTe$ crystals [and also in cadmium zinc telluride films and crystals, see Eqs (1) and (2)] is related to weakly controlled residual strains in them, arising mainly due to a large lattice mismatch between CdTe (6.4810 Å) and ZnTe (6.1037 Å) [21, 23]. A definite contribution to the discussed difference of $h\nu_m(A^0X)$ vs. x curves could bring disorder effects in $Cd_{1-x}Zn_xTe$ [9].

Evidently, application of "averaged" calibration curves $h\nu_m(A^0X) = \varphi(x)$ for $Cd_{1-x}Zn_xTe$ crystals results in a definite inaccuracy in obtained x values. This inaccuracy is shown in Fig. 3 and is of the order of ±11–15% for x = 0.03–0.35, ±5 – 10% for x = 0.35–0.75 and ±3 – 4% for x = 0.75–0.95. It significantly exceeds the inaccuracy occurring due to different types of shallow acceptors in $Cd_{1-x}Zn_xTe$ films and crystals (≤ 1%).

The reliability of the proposed $h\nu_m(A^0X)$ vs. x calibration curve for determination of $Cd_{1-x}Zn_xTe$ crystal composition is confirmed by a satisfactory correlation of x-values found directly from the X-ray microanalysis as well as using Eq. (2) (see Table 1A).

Note here that the residual strains in $Cd_{1-x}Zn_xTe$ alloys will also result in different $h\nu_m(D^0X)$ and $h\nu_m(X)$ values at fixed x for cadmium zinc telluride compounds obtained by various growth techniques (see Table 1 and Fig. 4). As expected, the pointed difference considerably exceeds that could be induced by shallow donors of different origin (± 1 meV, see, for example [27, 28]).

A note added in a proof

After the acceptance of the paper to publication, the following important works on E_g vs. x dependencies for $Cd_{1-x}Zn_xTe$ became known to the authors: $E_g = h\nu_m(A^0X) + 0.016\ \text{eV} = \varphi(x)$ at T = 4.2 K [32] (a relation between the room temperature intrinsic luminescence peak energy and A^0X band position at T = 4.2 K for $x \le 0.05$ is also given in [32]), and $E_g = \varphi(x)$ at T = 300 K [33,34].

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