CATHODOLUMINESCENCE STUDY
OF Cd\textsubscript{1-x}Mn\textsubscript{x}Te AND Zn\textsubscript{1-x}Mn\textsubscript{x}Te

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The cathodoluminescence spectra for Cd\textsubscript{1-x}Mn\textsubscript{x}Te (0 < x ≤ 0.7) and Zn\textsubscript{1-x}Mn\textsubscript{x}Te (0 < x ≤ 0.6) at room and liquid nitrogen temperature have been presented and discussed. Especially, the influence of increasing temperature and Mn content on cathodoluminescence spectra. The cathodoluminescence emission in Zn\textsubscript{1-x}Mn\textsubscript{x}Te (Cd\textsubscript{1-x}Mn\textsubscript{x}Te) centered at ≈ 1.95 eV (2.0 eV) and ≈ 2.2 eV (2.5 eV) are ascribed to Stokes-shifted $^4T_1(^4G) \rightarrow {^6}A_1(^6S)$ and $^4T_2(^4G) \rightarrow {^6}A_1(^6S)$ internal transitions of Mn$^{+2}$ within the 3$d^5$ state, respectively.

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The semiconducting compounds Cd\textsubscript{1-x}Mn\textsubscript{x}Te and Zn\textsubscript{1-x}Mn\textsubscript{x}Te belong to the family of diluted magnetic semiconductors DMSs [1]. Many investigations of Cd\textsubscript{1-x}Mn\textsubscript{x}Te and Zn\textsubscript{1-x}Mn\textsubscript{x}Te were carried out with applying different experimental and theoretical methods [1-6]. Today, it is clearly understood that for Cd\textsubscript{1-x}Mn\textsubscript{x}Te the fundamental energy gap increase linearly with Mn content [2, 3] in opposite to Zn\textsubscript{1-x}Mn\textsubscript{x}Te where deviation from linear behaviour in 0 < x ≤ 0.1 region of Mn content has been observed [4]. Moreover, it is possible to observe excitations and absorptions caused by intra Mn-ion transitions for both materials Cd\textsubscript{1-x}Mn\textsubscript{x}Te and Zn\textsubscript{1-x}Mn\textsubscript{x}Te. Unfortunately, till now luminescence of these materials under the electron beam has not been investigated and understood.

The cathodoluminescence measurements were carried out with employing the electron beam energy equal to 10 keV, electron current equal to 5 μA and transversal cross-section of the beam equal to 0.2 mm$^2$. The vacuum in the luminescence chamber was in the order of $10^{-7}$ Pa and the signal was detected using a standard grating monochromator and the lock-in technique. The samples used in our studies were prepared by the modified Bridgman method and manganese concentration x was checked by the electron microprobe analysis. The cathodoluminescence measurements were performed on natural cleaved surfaces.
The cathodoluminescence (CL) spectra obtained for mixed crystal $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ at 77 K (LNT) and 300 K (RT) are presented in Fig. 1a and 1b, respectively. In Fig. 2a CL spectra for $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ at LNT and in Fig. 2b at RT are presented. The energy position and the full width at half maximum (FWHM) of maxima $E_0$, $E_{M1}$ and $E_{M2}$ in CL spectra are deduced from approximately Gaussian band profiles. The $E_0$ maximum is associated with interband transition: conduction band $\rightarrow$ valence band, whereas the $E_M$ maxima are associated with internal transitions of $\text{Mn}^{2+}$ within the $3d^5$ state. As it can be seen from figures in both temperatures RT and LNT the increase in manganese content in crystals $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ and $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ is followed by the rise of the $E_0$ value. At LNT for $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ the change in the energy positions of this maximum as a function of Mn concentration is linear and equals $E_0^{\text{LNT}} = (1.37 \pm 0.04)x + 1.56 \pm 0.2$. Parameters of this linear equation are similar to those obtained by Vecchi et al. [3] for fundamental energy gap at 76 K using the photoluminescence measurements. It is worth noting that the FWHM of the $E_0$ maximum at LNT varies from $\approx 19$ meV for $x = 0.115$ to $\approx 72$ meV for $x = 0.7$ in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ and from $\approx 19$ meV for $x = 0.005$ to $\approx 49$ meV for $x = 0.532$ in $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$. Similar behaviour for $E_0$ maximum versus Mn content is observed in both ternary compounds at RT. Broadening of FWHM for $E_0$ is also observed due to the increase in temperature in both.

Fig. 1. The cathodoluminescence spectra for $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ obtained at (a) 77 K and (b) 300 K.
ternary compounds. The above facts as well as the non-linear changes of $E_0$ for Zn$_{1-x}$Mn$_x$Te imply the interband nature of the maximum $E_0$ observed in CL spectra. For Cd$_{1-x}$Mn$_x$Te at LNT, when the Mn concentration is higher than 0.34 an additional maximum $E_{M1}$ is observed. The energy position of this maximum does not change ($\approx 2$ eV) and also FWHM maintains the same value in the order of 130 meV. This indicates Mn intraion origin of the maximum $E_{M1}$ and we associated this maximum with Stokes-shifted $4T_1(4G) \rightarrow 6A_1(6S)$ transition within 3$d^5$ state. Note that for concentration higher than $x = 0.34$ the emission of approximately 2 eV related to localized Mn states dominates the CL spectra like in photoluminescence spectra [3]. For Cd$_{1-x}$Mn$_x$Te at LNT, the increase in fundamental gap due to Mn content does not cause in consequence subsequent internal $4T_2(4G) \rightarrow 6A_1(6S)$ transitions of Mn$^{2+}$ expected at $\approx 2.4$ eV, moreover $4T_1(4G) \rightarrow 6A_1(6S)$ transition still dominates in CL spectra. This situation is caused by an energy transfer mechanism from the excited Mn$^{2+}$ ions via the Mn sublattice to Mn ions in a disturbed environment [7] and directly reflects in CL spectra. Domination in the CL spectra of the intraion transitions with smaller energy, with the increase in the concentration of transition metals is also observed for iron at LNT [8]. Results obtained for Cd$_{1-x}$Mn$_x$Te in RT are rather unexpected. As it can be seen from Fig. 1b at RT for Mn concentration $x = 0.215$ there is observed the dominating maximum $E_0$ related

Fig. 2. The cathodoluminescence spectra for Zn$_{1-x}$Mn$_x$Te obtained at (a) 77 K and (b) 300 K.
to interband transition and two $E_{M_1}$ and $E_{M_2}$ maxima which should be associated to Stokes-shifted $^4T_1(^4G) \rightarrow ^6A_1(^6S)$, $^4T_2(^4G) \rightarrow ^6A_1(^6S)$ Mn intraion transitions. At LNT, for Zn$_{0.995}$Mn$_{0.005}$Te one can clearly distinguish two maxima $E_{M_1}$ and $E_{M_2}$ which are also related to the $^4T_1(^4G) \rightarrow ^6A_1(^6S)$ and $^4T_2(^4G) \rightarrow ^6A_1(^6S)$ transitions, respectively. From their energy positions for the Racah parameters ratio $C/B = 4.48$ the crystal field splitting parameters $D_q = 720 \text{ cm}^{-1}$ have been calculated. At RT for Zn$_{0.995}$Mn$_{0.005}$Te, Mn intraion transitions are dominated by interband transitions occurring for the same energy. Similar, as for Cd$_{1-x}$Mn$_x$Te in Zn$_{1-x}$Mn$_x$Te for concentration $x > 0.1$ dominating role in the CL is played by, for the reason mentioned earlier, transitions $^4T_1(^4G) \rightarrow ^6A_1(^6S)$, which make other deexcitation processes ineffective. It is worth noting that for high content of Mn its atomic nature is lost and transitions observed in CL will take place to the Mn bands rather than to the atomic states.

References