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CATHODOLUMINESCENCE STUDY OF $Cd_{1-x}Mn_xTe$ AND $Zn_{1-x}Mn_xTe$

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The cathodoluminescence spectra for $Cd_{1-x}Mn_xTe$ ($0 < x \leq 0.7$) and $Zn_{1-x}Mn_xTe$ ($0 < x \leq 0.6$) 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 $Zn_{1-x}Mn_xTe$ ($Cd_{1-x}Mn_xTe$) centered at ≈ 1.95 eV (2.0 eV) and ≈ 2.2 eV (2.5 eV) are ascribed to Stokes-shifted ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$ and ${}^4T_2({}^4G) \rightarrow {}^6A_1({}^6S)$ internal transitions of Mn^{+2} within the $3d^5$ state, respectively.

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The semiconducting compounds $Cd_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xTe$ belong to the family of diluted magnetic semiconductors DMSs [1]. Many investigations of $Cd_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xTe$ were carried out with applying different experimental and theoretical methods [1-6]. Today, it is clearly understood that for $Cd_{1-x}Mn_xTe$ the fundamental energy gap increase linearly with Mn content [2, 3] in opposite to $Zn_{1-x}Mn_xTe$ where deviation from linear behaviour in $0 < x \leq 0.1$ 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 $Cd_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xTe$. 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.

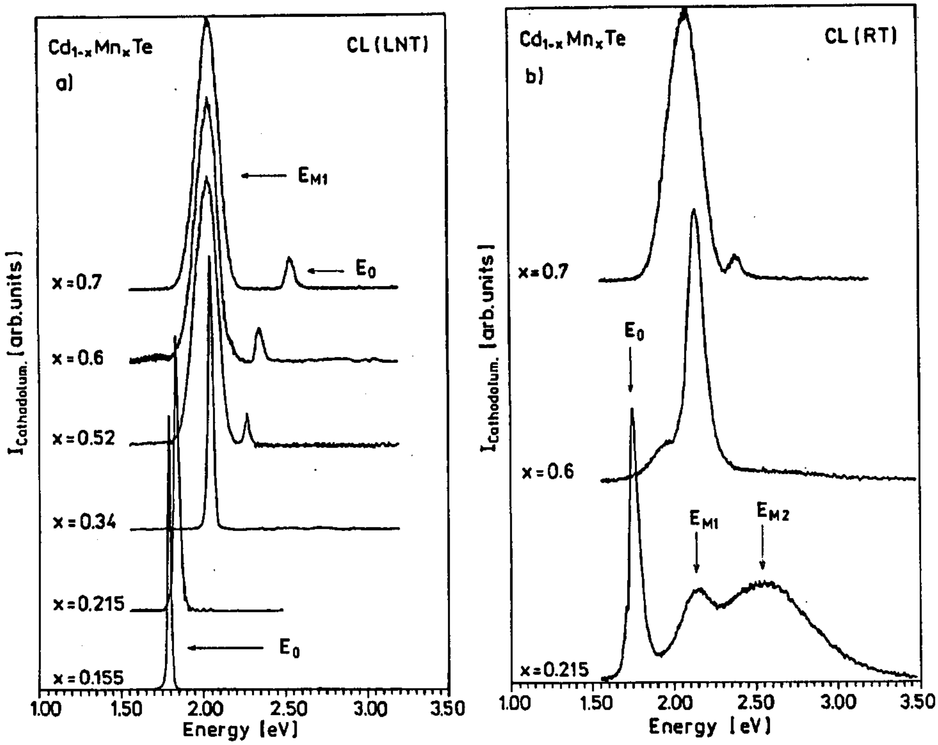

Fig. 1. The cathodoluminescence spectra for $Cd_{1-x}Mn_xTe$ obtained at (a) 77 K and (b) 300 K.

The cathodoluminescence (CL) spectra obtained for mixed crystal $Cd_{1-x}Mn_xTe$ at 77 K (LNT) and 300 K (RT) are presented in Fig. 1a and 1b, respectively. In Fig. 2a CL spectra for $Zn_{1-x}Mn_xTe$ 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 → valence band, whereas the E_M maxima are associated with internal transitions of 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 $Cd_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xTe$ is followed by the rise of the E_0 value. At LNT for $Cd_{1-x}Mn_xTe$ the change in the energy positions of this maximum as a function of Mn concentration is linear and equals $E_0^{\mathrm{LNT}} = (1.37 \pm 0.04)x + 1.56 \pm 02$. 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 $Cd_{1-x}Mn_xTe$ and from $\approx$ 19 meV for $x = 0.005$ to $\approx$ 49 meV for $x = 0.532$ in $Zn_{1-x}Mn_xTe$. 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

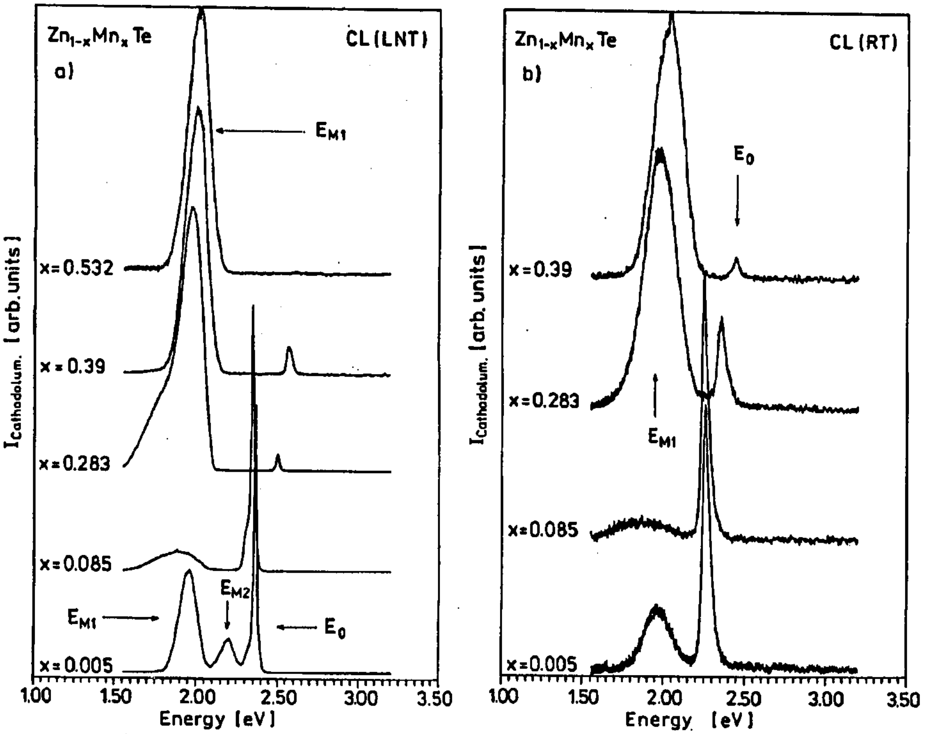

Fig. 2. The cathodoluminescence spectra for $Zn_{1-x}Mn_xTe$ obtained at (a) 77 K and (b) 300 K.

ternary compounds. The above facts as well as the non-linear changes of E_0 for $Zn_{1-x}Mn_xTe$ imply the interband nature of the maximum E_0 observed in CL spectra. For $Cd_{1-x}Mn_xTe$ 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 $3d^5$ 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 $Cd_{1-x}Mn_xTe$ 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 $Cd_{1-x}Mn_xTe$ 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 to interband transition and two E_{M1} and E_{M2} maxima which should be associated to Stokes-shifted ${}^4T_1({}^4G) \to {}^6A_1({}^6S)$, ${}^4T_2({}^4G) \to {}^6A_1({}^6S)$ Mn intraion transitions. At LNT, for $\mathrm{Zn_{0.995}Mn_{0.005}Te}$ one can clearly distinguish two maxima E_{M1} and E_{M2} which are also related to the ${}^4T_1({}^4G) \to {}^6A_1({}^6S)$ and ${}^4T_2({}^4G) \to {}^6A_1({}^6S)$ transitions, respectively. From their energy positions for the Racah parameters ratio $C/B = 4.48$ the crystal field splitting parameters $Dq = 720$ cm^{-1} have been calculated. At RT for $\mathrm{Zn_{0.995}Mn_{0.005}Te}$, Mn intraion transitions are dominated by interband transitions occurring for the same energy. Similar, as for $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ in $\mathrm{Zn}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ for concentration $x > 0.1$ dominating role in the CL is played by, for the reason mentioned earlier, transitions ${}^4T_1({}^4G) \to {}^6A_1({}^6S)$, 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.

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