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## ENERGY STATES OF Ni IN $Zn_{1-x}Mn_xSe:Ni$ SOLID SOLUTIONS

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Absorption and reflectivity measurements were carried out on  $Zn_{1-x}Mn_xSe:Ni$  solid solutions. The spectra demonstrate the radical change of the structure of internal  $Ni^{2+}(3d^8)$  transitions at the presence of the Mn ions and strong dependence on Mn concentration. The threshold energy  $\hbar\omega_{th}$  for the process of Ni photoionization to the valence band  $Ni^{2+}(3d^8) + \hbar\omega_{th} \rightarrow Ni^{1+}(3d^9) + h$  is shifted to the lower energy by  $\approx 30$  meV, but hardly depends on  $x$  despite the essential increase in the energy gap.

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Absorption spectra of II-VI semiconductors doped with 3d transition metal ions usually demonstrate both intra-configuration  $d-d$  transitions and broad charge transfer band due to impurity photoionization. In  $ZnSe:Ni$  one observes besides  $Ni^{2+}(3d^8)$  internal absorption [1] a strong absorption band below the band-gap energy which is attributed to the process of Ni photoionization to the valence band  $Ni^{2+}(3d^8) + \hbar\omega_{th} \rightarrow Ni^{1+}(3d^9) + h$  [2-4]. The threshold energy  $\hbar\omega_{th}$  gives the energy position of  $Ni^{1+}$  ion with respect to the valence band.

It seems interesting to investigate how the extremely large exchange interactions typical of  $Zn_{1-x}Mn_xSe$  even in the absence of applied magnetic field [5] modify the energies of Ni states.

The single crystals used in this study were grown by Bridgman method. Manganese and nickel were added to the melt, corresponding to a Ni concentration of  $6 \times 10^{17} \text{ cm}^{-3}$  for all samples and Mn molar fraction from  $x = 0.0$  to 0.30. The majority of samples were freshly cleaved, the remainder were polished. The samples were mounted on a copper cold finger attached to a helium bath. Absorption and reflection spectra were recorded with DFS-monochromator with a photomultiplier tube connected to a photon counting system [6].

The investigated samples are listed in Table. Reflectivity measurements (Fig. 1) were undertaken in order to establish band-gap energies for the samples. The point  $R_{1/2} = (R_{max} + R_{min})/2$  was used to characterize the free exciton

TABLE  
Free exciton energies  $E_{FE}$  and threshold energies  $\hbar\omega_{th}$  for  $Ni^{2+}$  photoionization process for studied  $Zn_{1-x}Mn_xSe:Ni$  crystals at 5 K. Ni concentration is equal to  $6 \times 10^{17} \text{ cm}^{-3}$  for all samples.

$X$	$E_{FE}$ [eV]	$\hbar\omega_{th}$ [eV]
0.0	2.802	1.850
0.033	2.798	1.816
0.190	2.906	1.805
0.157	2.840	1.816
0.178	2.900	1.816
0.372	—	1.816

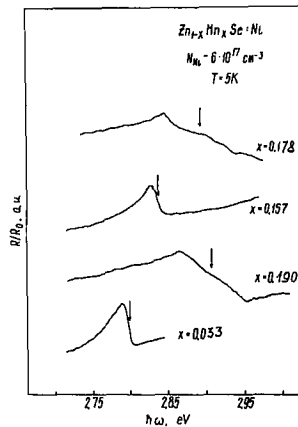


Fig. 1. Reflectivity spectra of  $Zn_{1-x}Mn_xSe:Ni$  crystals at 5 K.

energy, where  $R_{max}$  and  $R_{min}$  are maximum and minimum of the reflection coefficient in the region of the excitonic structure. The values  $E_{FE}$  are listed in Table. We note that reflectivity features seen by us in  $Zn_{1-x}Mn_xSe:Ni$  are not identical to the published spectra for  $Zn_{1-x}Mn_xSe$  [5, 7].

Absorption spectra were obtained in the range 1.5–2.1 eV (Figs. 2, 3). A broad charge transfer band due to Ni photoionization to the valence band  $Ni^{2+}(3d^8) + \hbar\omega_{th} \rightarrow Ni^{1+}(3d^9) + h$  is observed for all crystals. There is no fine structure near the threshold energy connected with bound “acceptor” excitons  $[Ni^{1+}h]$ , which is usually observed in  $ZnSe:Ni$  [2–4]. Figure 2 shows data for the plot  $\alpha^{2/3}$  against  $\hbar\omega$ , which is a straight line with intercept  $\hbar\omega_{th}$ , i.e. the ionization energy [4]. The threshold energies  $\hbar\omega_{th}$  are listed in Table.

The value  $\hbar\omega_{th} = 1.850$  eV for  $ZnSe:Ni$  ( $x = 0.0$ ) is consistent with previous results [3, 4]. From Fig. 2 it can be seen that excluding sample with  $x = 0.05$  the

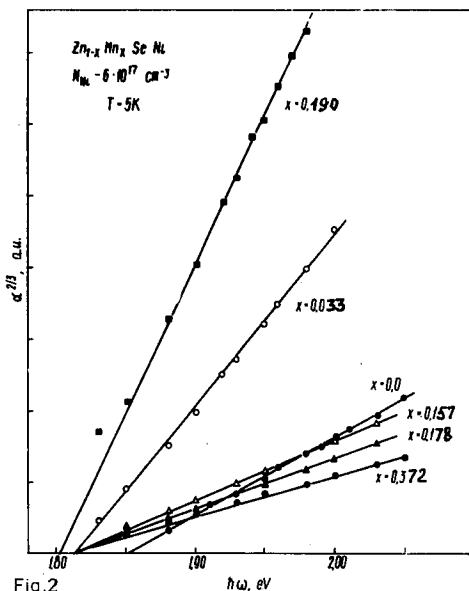


Fig. 2

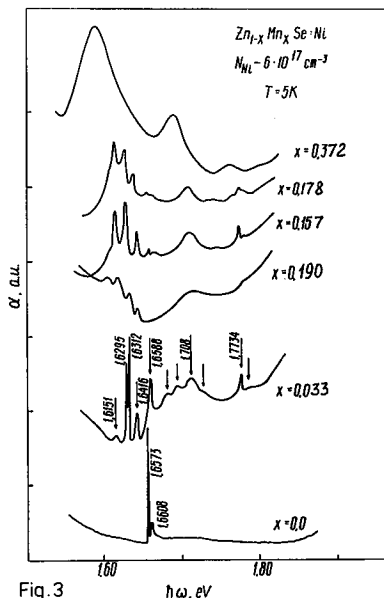


Fig. 3

Fig. 2. Absorption data near the threshold of  $Ni^{2+}$  photoionization band of  $Zn_{1-x}Mn_xSe:Ni$  crystals. Full squares,  $\circ$ ,  $\bullet$ ,  $\Delta$ , full triangles, semi-full circles — experimental points for the samples with different  $x$ .

Fig. 3. Low temperature absorption spectra of  $Zn_{1-x}Mn_xSe:Ni$  crystals in  $Ni^{2+}$   $d-d$  transition band.

behaviour of  $\hbar\omega_{th}$  versus  $x$  is as follows: there is an initial decrease in the energy by  $\approx 30$  meV in comparison with  $ZnSe:Ni$  followed by an independence of  $\hbar\omega_{th}$  on  $x$ . This independence of threshold energy for the process of  $Ni^{2+}$  photoionization to the valence band, despite the essential increase in the energy gap with  $x$  for these samples, may indicate an independence on the absolute energy scale of the position of the valence band in the  $Zn_{1-x}Mn_xSe$  solid solution.

The initial drop of  $Ni^{1+}(3d^9)$  state energy may be explained as the result of  $Ni-Mn$  complexes formation and strong exchange interactions in these crystals. It seems that the dramatical change of the structure of the internal  $Ni^{2+}(3d^8)$  transitions (Fig. 3) confirms this idea. Instead of the two narrow lines attributable exactly to  $Ni^{2+}(3d^8) \ ^3T_1(F) \rightarrow \ ^1T_2(G)$  transitions in  $ZnSe:Ni$  we observe the complicated structure in  $Zn_{1-x}Mn_xSe:Ni$  solid solutions. With incorporation of more Mn all peaks broaden but their intensity changes slightly except the peak corresponding to the initial one of  $ZnSe:Ni$ . This peak disappears already at  $x = 0.05$ . It may be connected also with the local deviation from  $T_d$  symmetry in solid solutions  $Zn_{1-x}Mn_xSe$  [8]. Further investigations, first of all EPR measurements are necessary to be done to clear up the behaviour of Ni states in the solid solutions.

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