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LIQUID NITROGEN TEMPERATURE REFLECTIVITY SPECTRA OF $Zn_{1-x}Mn_xSe$ AND $Zn_{1-y}Fe_ySe$ MIXED CRYSTALS

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The liquid nitrogen temperature reflectivity spectra of the tetrahedral diluted magnetic semiconductors (DMS's) $Zn_{1-y}Fe_ySe$ and $Zn_{1-x}Mn_xSe$ crystallizing in the zinc-blende structure were investigated. The reflectivity measurements for different concentration of Fe ($y = 0.01$, 0.05, and 0.10) and Mn ($x = 0.10$ and 0.30) ions were taken out in a wide energy range between 4 and 30 eV using synchrotron radiation from ADONE storage ring in Frascati. The average resolution $\Delta E/E$ used for these measurements was better than 1×10^{-3} over the entire spectral range. The single crystals were cleaved, before being mounted inside the reflectometer, from the samples grown by the Bridgman method. The comparison between the reflectivity spectra of ternary systems and host crystal ZnSe is made. The changes of the structures of reflectivity spectra of host crystal ZnSe caused by the influence of Fe and Mn ions are discussed.

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$Zn_{1-x}Mn_xSe$ and $Zn_{1-y}Fe_ySe$ ternary semiconducting compounds belong to the materials often referred to as semimagnetic semiconductors (SMSC's) or the diluted magnetic semiconductors (DMS) which are characterized by the unique combination of semiconducting and magnetic properties [1]. The latter originate from the open shell of $3d$ transition metal electrons. $Zn_{1-x}Mn_xSe$ ($0 < x < 0.35$) [2] and $Zn_{1-y}Fe_ySe$ ($0 < y < 0.22$) [3] single crystals with tetrahedrally ordinated zinc-blende (ZB) symmetry can be grown as the crystalline one-phase ternary compounds. There are many interesting phenomena observed in semiconducting semimagnetic materials. Unfortunately, a detailed understanding of the electronic structure of these materials is still not complete. A band structure study of ZnSe, the parent binary compound of ZnMnSe and ZnFeSe, has shown that this semiconducting compound is characterized by a large and direct energy gap [4]. In comparison with the well-known band structure of ZnSe [5], the information about the band structure of ZnSe based ternary compounds with the transition metals Mn and Fe is less well understood. Recently, ZnMnSe and ZnFeSe DMS's have attracted considerable attention as a result of the large exchange interaction between the band electrons and the d electrons of Fe or Mn ions, the so-called sp–d superexchange interaction [6, 7]. On the basis of these spin exchange interactions in ZnMnSe/ZnFeSe multiple-quantum-well structures have been created and studied [8]. The aim of this paper is to present the reflectivity measurements of ZnMnSe, and ZnFeSe in the 4–25 eV energy range at the liquid nitrogen temperature.

The reflectivity measurements were performed at the vacuum ultraviolet beamline of PULS laboratories at INFN Frascati National Laboratories. Synchrotron radiation from the ADONE storage ring was focused onto the entrance slit of a 1 m near normal incidence monochromator. The average resolution $\Delta E/E$ used for these measurements was better than 1×10^{-3} over the entire spectral range. The $Zn_{1-x}Mn_xSe$ ($x = 0.10$ and 0.30) and $Zn_{1-y}Fe_ySe$ ($y = 0.01$, 0.05 and 0.10) single crystals were cleaved before being mounted inside the reflectometer fromingots grown by the Bridgman method. The samples were attached to the cold finger of a liquid nitrogen temperature (LNT) cryostat. Data acquisition was done by means of a lock-in amplifier whose output was digitized and fed into the setup control computer.

Figures 1a and 1b present the experimental reflectivity spectra for $Zn_{1-x}Mn_xSe$ ($x = 0.10$ and 0.30) at liquid nitrogen temperature in two different energy ranges; Figs. 2a and 2b show the reflectivity spectra for $Zn_{1-y}Fe_ySe$ ($y = 0.01$, 0.05 and 0.10) at LNT. In all the figures the ZnSe reflectivity spectrum has been presented for comparison. A general analysis of the reflectivity spectra for $Zn_{1-x}Mn_xSe$ and $Zn_{1-y}Fe_ySe$ shows that they are similar in shape to the spectrum of pure ZnSe. With increasing Mn or Fe content, in the ZnMnSe or ZnFeSe, the fine structures observed in ZnSe spectrum are smeared, particularly quickly in the low energy range (4–10 eV) (see Figs. 1a and 2a). The peaks E_1 and $E_1 + \Delta_1$ (in Cardona's notation) assigned to the transitions in the Λ direction of Brillouin zone (BZ) are smeared as well as shifted to lower energies in the case of ZnMnSe and to higher energies for ZnFeSe. This latter behavior of the E_1 and $E_1 + \Delta_1$ transitions has been theoretically anticipated on the basis of the semi-empirical tight binding band structure calculations and experimentally confirmed by Kim et al. [9]. Also

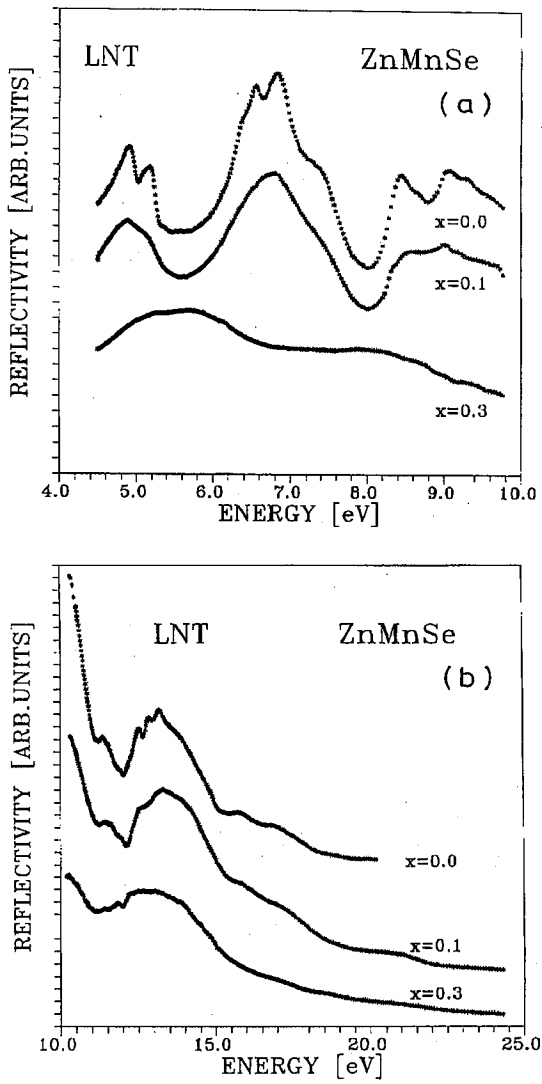

Fig. 1. The reflectivity spectra of $Zn_{1-x}Mn_xSe$ ($x = 0.0$, 0.1 and 0.3) at liquid nitrogen temperature: (a) 4–10 eV energy range, (b) 10–25 eV energy range.

the maximum E_2, both in ZnMnSe and ZnFeSe, loses its fine structure as well as its intensity. For 30% of Mn content the maximum E_2 completely disappears (see Fig. 1a). A similar smearing is observed also for the structures at 8.40 eV which have been assigned to the transition at L point of BZ [5] (E_1' transition) as well as for the peak at 9.06 eV [5], identified by Walter and Cohen [10] as transitions in several critical points of the BZ volume.

In the 10–25 eV energy range, where in the spectrum of ZnSe, the structures have been interpreted as transitions from the Zn $3d$ core state to the conduction

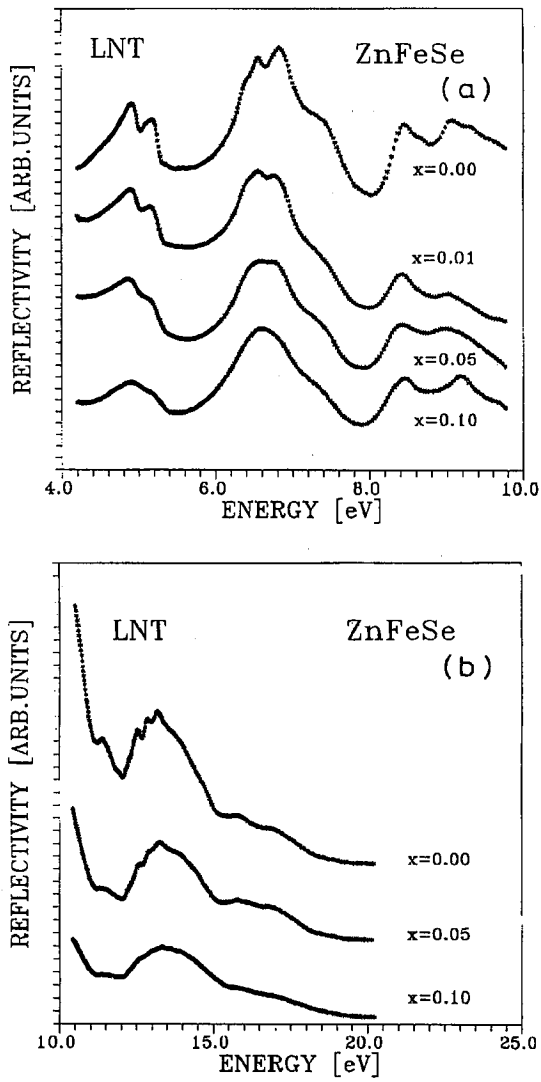

Fig. 2. The reflectivity spectra of $Zn_{1-y}Fe_ySe$ (x = 0.00, 0.01, 0.05 and 0.10) at liquid nitrogen temperature: (a) 4–10 eV energy range, (b) 10–25 eV energy range.

band in various points of the BZ [5], the influence of increasing Mn or Fe content is not so large as in the low energy range. The main structures present in this energy range identified earlier for ZnSe [5] are observed also in ZnFeSe as well as in ZnMnSe with 10% Mn content. However, for samples with 30% of Mn content only the same general shape of the spectrum remains. An important contribution of Mn or Fe ions seems to cause a shift to higher energies of the broad band with the maximum localized at about 13.5 eV. This effect is well seen in Fig. 3 where the normalized spectra of ZnMnSe (10% Mn content), ZnFeSe (10% Fe content) and

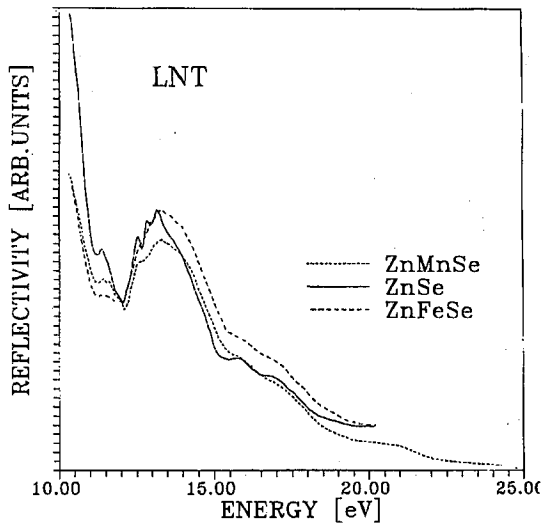

Fig. 3. The comparison between the normalized spectra of pure ZnSe, $Zn_{0.9}Mn_{0.1}Se$ and $Zn_{0.9}Fe_{0.1}Se$ in high energy range 10–25 eV.

ZnSe in the energy range 10–25 eV are compared. This behavior of the reflectivity spectra could be assigned to transitions from the Zn $3d$ states to the empty t_2 states of Mn or Fe, hybridized with the conduction band p-like states and located 2–3 eV above the bottom of the conduction bands, as already found in other II–VI ternary compounds with Mn [11]. However, it could be also correlated with the recent results of the X-ray absorption near-edge structure (XANES) analysis for the unoccupied states of ZnMnSe and ZnFeSe which present a significant contribution of the ZB MnSe or ZB FeSe p-like DOS in conduction band around 11.8 eV and 9.6 eV above the bottom of the conduction band, respectively [12].

In conclusion, the studies of the fundamental reflectivity spectra of ZnMnSe and ZnFeSe ternary compounds in 4–25 eV energy range at liquid nitrogen temperature explain the influences of transition metals on the band structure of host crystal. With increase in the Mn content in ZnMnSe and Fe content in ZnFeSe the fine structure of the reflectivity spectrum observed in ZnSe [5] is smeared and finally for 30% of Mn this fine structure disappears. This effect is correlated with the influence of the hybridization of the $3d$ states of Mn and Fe as well as with the topological disorder in ternary compounds. The significant influence of the Mn and Fe $3d$ states, on the high energy range spectrum (10–25 eV), has been associated with additional contribution of the hybridized unoccupied $3d$ states of Mn or Fe with conduction bands of ZnSe host crystal.

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