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ROOM AND LIQUID NITROGEN TEMPERATURE REFLECTIVITY SPECTRA OF $Zn_{1-x}Co_xSe$ MIXED CRYSTALS*

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The optical properties of the semiconducting compounds $Zn_{1-x}Co_xSe$ crystallizing in the zinc-blende structure have been investigated. The reflectivity spectra of these materials for different concentration of Co ions, have been taken out in a wide energy range between 4 and 25 eV at room (RT) and liquid nitrogen temperature (LNT) using synchrotron radiation from ADONE Storage Ring in Frascati. The comparisons between the reflectivity spectra of ternary systems and host crystal ZnSe are made. On the basis of the experimental and theoretical results, the changes of the structures of the reflectivity spectra of host crystal ZnSe caused by the influence of transition metal ions are discussed.

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The ternary compounds $Zn_{1-x}Co_xSe$ belong to the group of materials known as diluted magnetic semiconductors (DMSs), in which the transition metal ions (Mn, Fe, Co) randomly replace some of cations (Zn, Hg, Cd) in the II–VI semiconductor lattice. Due to their important semiconducting as well as magnetic properties, DMSs have been the subject of extensive studies [1]. While the intrinsic

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properties of Mn- and Fe-based DMSs are nowadays reasonably well understood, the situation is quite different for Co-based compounds. Results on magnetic properties of $Zn_{1-x}Co_xSe$ have been recently reported [2, 3], giving information about large exchange constant in the Co-based DMSs arising from efficient hybridization of the d-states with the valence band [4]. The optical absorption and photoluminescence spectra [5] show the transitions between the different energy levels of Co^{2+} ions for the states of d^7 configuration in a crystal field of T_d symmetry characteristic of zinc-blende structure.

The predominant part of the physical properties of the DMSs, in our case ZnSe with Co, depends on the location of the Co^{2+} ($3d^7$) states and their hybridization with the valence band electrons of the host crystal ZnSe [6, 7]. The spectra measured for $Zn_{1-x}Co_xSe$ will be compared to the reflectivity spectrum obtained for a pure ZnSe crystal. So far in the literature only RT reflectivity data (2–12 eV) for this compound are reported [8].

The RT and LNT reflectivity measurements were performed at the vacuum ultraviolet beam line 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 equipped with two gratings interchangeable under vacuum conditions. The average resolution $\Delta E/E$ used for these measurements was better than 1×10^{-3} over the entire spectral range. The $Zn_{1-x}Co_xSe$ ($x = 0.00$, 0.01, 0.03, and 0.05) samples, grown by the modified Bridgman method, were washed in alcohol before being mounted inside the reflectometer chamber. The crystals were attached to the cold finger of a LNT cryostat. Data acquisition was done by means of a lock-in amplifier whose output was digitized and fed into the set-up control computer.

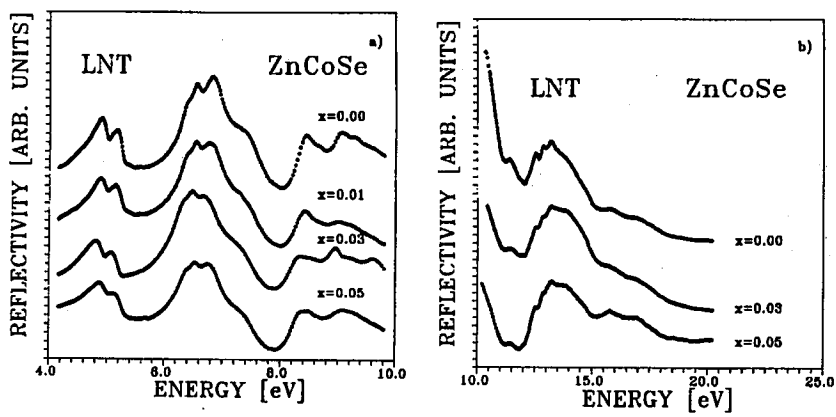

Fig. 1. The reflectivity spectra of $Zn_{1-x}Co_xSe$ taken out in a wide energy range at LNT; (a) a low energy range of 4–10 eV; (b) a high energy range of 10–25 eV.

Figures 1a and 1b show the reflectivity spectra of $Zn_{1-x}Co_xSe$ ($x = 0.00$, 0.01, 0.03, 0.05) taken out at LNT in a wide energy range of 4–25 eV. Generally, the presence of Co ions leads to some changes in the relative intensities of the

reflectivity structures as well as to some shifts in the energy positions of the reflectivity maxima. The maxima E_1 and $E_1 + \Delta_1$ (for pure ZnSe appeared at 4.88 eV and 5.13 eV [7]), originated from the transitions along Λ direction near L point in Brillouin zone (BZ), became both less pronounced and smeared, and shifted towards higher energies with an increase in x. The split E_2 maximum, assigned to the transitions in a large volume of BZ and also along Δ direction, does not seem to move in energy position when the Co ions replace Zn ones in cation sublattice. The E_0' shoulder (7.24 eV) corresponding to transitions near Γ and along Δ direction is well pronounced even for the highest measured Co content. The E_1' and $E_1' + \Delta_1'$ structures (8.40 and 9.06 eV) arised from transitions near L point are consequently blurred. At energies above 10 eV the reflectivity structure is associated with the transitions involving the core levels of Zn $3d$ and Se $4s$. The origin of this energy range maxima for ZnSe has been widely discussed and explained by Markowski et al. [7]. The energy positions of these maxima, while adding Co ions, do not change significantly but their relative intensities decrease. It could be caused by the changes in conduction bands states distribution caused by the presence of Co states. The spectra presented in Figs. 2a and 2b for RT are less structured in comparison with the LNT spectra, showing the normal behaviour of semiconducting compounds [9]. The influence of increasing Co content is demonstrated by blurring reflectivity structures and shifting of the energy positions of maxima.

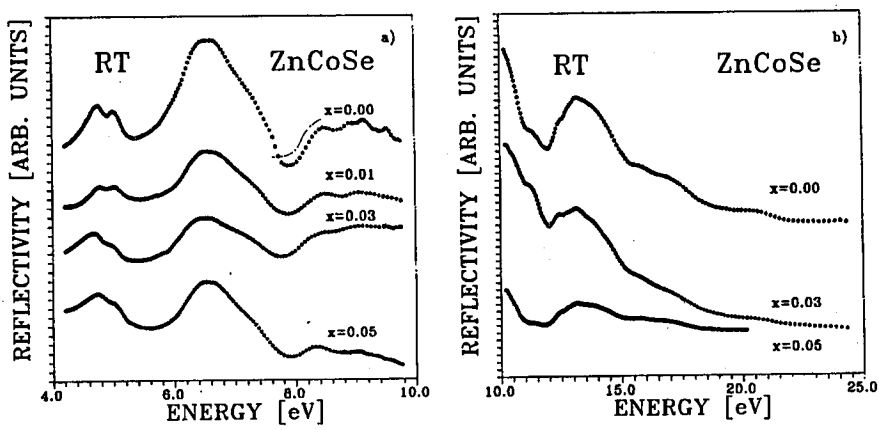

Fig. 2. The reflectivity spectra of $Zn_{1-x}Co_xSe$ taken out in a wide energy range at RT; (a) a low energy range of 4–10 eV; (b) a high energy range of 10–25 eV.

In conclusion, the studies of the reflectivity spectra of $Zn_{1-x}Co_xSe$ ternary compounds in the 4–25 eV energy range show that the influence of Co presence is much more visible in the low energy range than in the high energy region where the transitions from core levels to CB occur. This seems to be reasonable assuming the location of Co states in the valence band of host crystal alike for other transition metals (Mn, Fe).

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