

VACUUM ULTRAVIOLET REFLECTIVITY OF $\text{Cd}_{1-x}\text{Fe}_x\text{Te}^*$

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Reflectivity spectra for mixed crystals $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ with $0.00 \leq x \leq 0.05$ were investigated. The measurements were carried out in the energy range 6.0–30.0 eV at 300 K. The influence of $\text{Fe}^{2+}(3d^6)$ states on the changes in the energy positions of the reflectivity maxima E'_1 , $E'_1 + \Delta$, c , d , e , f , h and i is analysed. The obtained results confirm the band structure diagrams published previously.

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The mixed crystals $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ belong to the group of materials known as diluted magnetic semiconductors (DMS). Because of their important semiconducting and magnetic properties [1], DMS have recently been the subject of extensive studies. These ternary systems contain magnetic atoms which randomly replace some of cations in the II–VI semiconductor lattice. The predominant part of the physical properties of DMS, in our case CdTe with Fe, depends on the location of the $\text{Fe}^{2+}(3d^6)$ states relatively to the top of the valence band (VB) or to the bottom of the conduction band (CB). The optical properties of these compounds were previously studied using absorption [2] and reflectivity measurements [3–6]. Changes in the shapes of the measured reflectivity spectra, caused by the influence of the Fe content, were observed. The experimental results obtained by Sarem et

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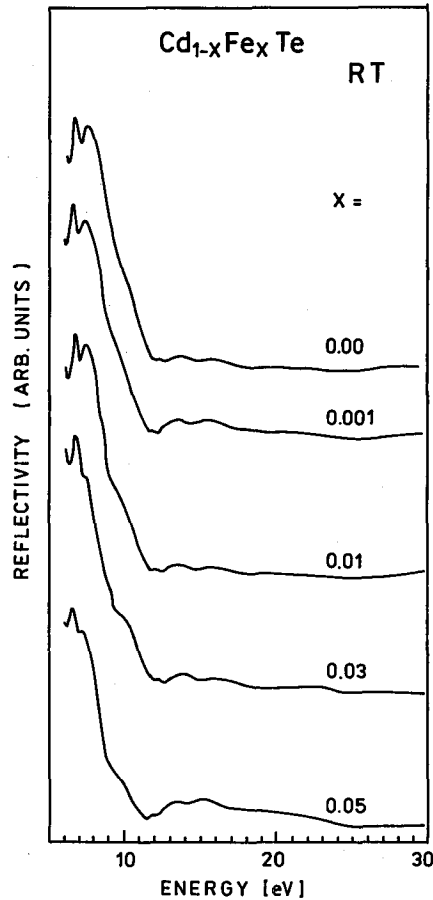


Fig. 1. Reflectivity spectra for $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ in the 6–30 eV energy range performed at 300 K (RT).

al. [4] were compared with the calculated band structure of the host crystals [7, 8]. All the collected results allowed to extend [4] the band structure diagrams [9–11] of these compounds.

In this paper we present the reflectivity measurements performed for the $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ ternary systems. Dependences of the high-energy maxima positions on Fe concentration are studied. The influence of $\text{Fe}^{2+}(3d^6)$ states and their *s-p-d* hybridization with the bands of the host crystal makes it possible to explain the behaviour of changes in the shape and in the energy positions of other maxima in reflectivity spectra.

The ternary system $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ crystallizes in the zinc-blende structure for $x \leq 0.06$ [12] with the Fe^{2+} ions replacing Cd^{2+} at random lattice sites. The incompatibility of the NiAs structure, in which FeTe crystallizes, with the zinc-blende structure of CdTe imposes an upper limit on x .

The monocrystalline samples of $Cd_{1-x}Fe_xTe$ ($0 \leq x \leq 0.05$) used in our studies were prepared by the modified Bridgman method using individual elements as starting materials. The samples were cleaved and their surfaces were cleaned with methyl alcohol just before the experiment. The lattice constant d was determined at room temperature (RT) by X-ray powder diffraction, using the Debye-Scherrer method, giving the linear dependence $d(x)$. The iron concentration was checked by microprobe (precision better than 0.001). The reflectivity measurements of $Cd_{1-x}Fe_xTe$ crystals were carried out in the 6–30 eV energy range at RT with the use of synchrotron radiation available at the vacuum ultraviolet beam line at the PULS facility in Frascati [13]. The average resolution of the setup was 1–2 Å over the entire energy range.

The reflectivity spectra of $Cd_{1-x}Fe_xTe$ in the energy range between 6 and 30 eV are presented in Fig. 1. The shapes of spectra were affected by the samples quality and the surface preparation. Variations as large as ± 0.01 eV of the energies of the reflectivity structures were noticed while studying different samples.

In the reflectivity spectra in the ultraviolet region one can distinguish E'_1 and $E'_1 + \Delta$ maxima (Fig. 1) related to the transitions between the spin-orbit split highest valence band ($L_{4,5}, L_6$) and second conduction bands ($L_6, L_{4,5}$) in the vicinity of the L critical point along the Λ direction [14]. The initial states of these transitions are the same as in the case of E_1 and $E_1 + \Delta_1$ maxima, therefore, one can expect a similar energy dependence. The energy position of E'_1 maximum with increasing Fe content remains almost unchanged like for E_1 maximum and the explanation of such behaviour suggested for E_1 and $E_1 + \Delta_1$ maxima [15] seems to be applicable here, as well. However, the energy position of $E'_1 + \Delta$ changes in different way, which should be connected with the nature of final states. Kisiel et al. [16], using a virtual crystal model for the hypothetical zinc-blende FeTe for the interpretation of XANES experiment, extracted the projected s -, p -, and d -like density of states (DOS) of FeTe in $Cd_{1-x}Fe_xTe$. They found that the extracted DOS occupy presumably the bottom of CB (p -like DOS) and the position 5 eV above it (s -, d -like DOS). The latter s - and d -like states could eventually disturb the final state of the interband transitions. The detailed analysis of $E_1 + \Delta_1$ energy positions [15] with Fe concentration indicated also some small deviation from the straight-line dependence.

In the reflectivity structure of pure CdTe near 10.4 eV there is a shoulder associated with the transitions from the third valence band ($L_6^{(2)}$) to the second lowest conduction band ($L_6^{(2)}$), which becomes more visible when the Fe content increases (Fig. 1). This feature should be connected with the influence of the Fe states in two different regions of the electronic band structure of these compounds. The final state $L_6^{(2)}$ is likely to be disturbed, according to the symmetry of these states, by empty states of FeTe indicated in XANES experiment [16]. On the other hand, from the photoemission data [17] it is known that the $3d$ state of e -symmetry is placed next to initial state (3.6 eV below the top of the VB). This additional iron states are likely to lead to an increase in a joint density of states for the mentioned above transitions to the second lowest conduction band $L_6^{(2)}$.

There are some different explanations in the literature on the origin of the

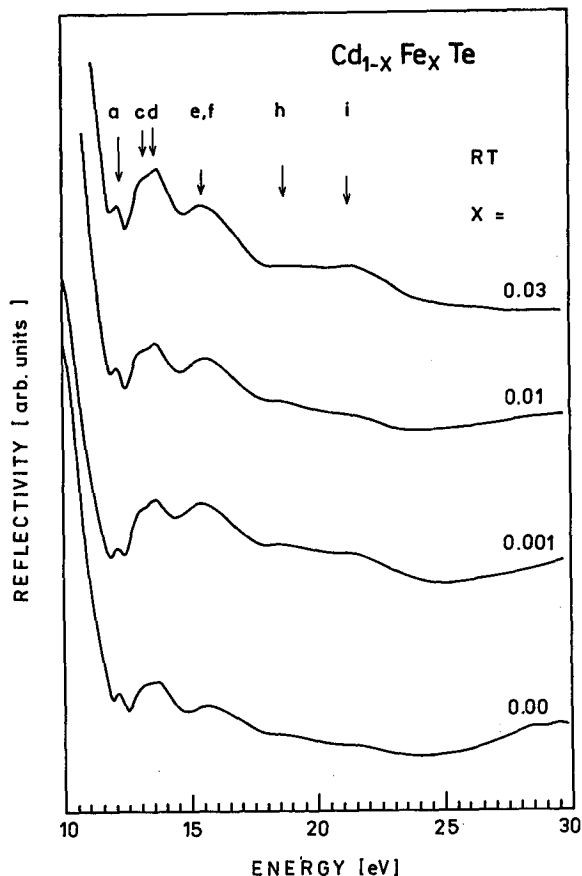


Fig. 2. Reflectivity spectra for $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ in the 10–30 eV energy range performed at 300 K (RT).

α -maximum appearing for pure CdTe at about 12.13 eV. Kisiel et al. [13] interpreted it as a core exciton of the $4d_{5/2}$ level of cadmium in contrary to Krause and Gumlich's [18] interpretation, who connected this maximum with a transition from the $5s$ states of tellurium. On the other hand, according to the very recent LMTO band structure calculations [19], the main contribution to the α -peak could come also from the band-to-band transitions, i.e. from the two highest valence bands to the fifth conduction band. However, taking into consideration the broadening of the reflectivity maxima depending on the lifetime of initial and final states with many-body corrections [20] associated with given transitions, the contribution of the band-to-band transition to the α -peak becomes so small [21] that the explanation of the origin of α -peak as a core exciton should not be excluded. Looking over the behaviour of this maximum in our reflectivity spectra (Figs. 2 and 3), one can notice the independence of its energy position on iron concentration. Therefore,

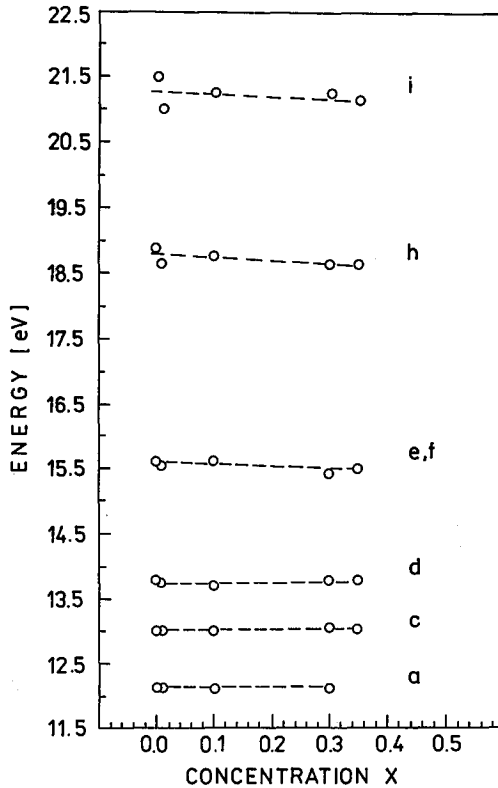


Fig. 3. Energy positions of the maxima *a*, *c*, *d*, *e*, *f*, *h*, and *i* as a function of Fe concentration.

both interpretations, as the core exciton and as the band-to-band transitions, are possible.

The next *c*, *d*, *e* and *f* maxima (Fig. 2) occur in CdTe at the energies 13.08, 13.77, and 15.63 eV respectively, with *e* and *f* not separated from each other. Figure 3 illustrates the shifts in energy positions of these maxima with Fe content changing. Such a similar behaviour is almost clear, assuming the assignment of these peaks to transitions from the same initial states $d_{5/2}$ of Cd to X_6 , DOS, Γ_7 and $L_6^{(2)}$ bands respectively [13]. Other authors [18, 22] associate the *c* reflectivity maximum in pure CdTe with different transitions. Krause and Gümlich [18] assigned it to the core exciton. In all cadmium chalcogenides Freeouf [22] found a doublet, *c* and *d* in our notation, split by about 0.6 eV. The fact that the energy of splitting does not change upon going from the sulfide to telluride implies that the splitting is intrinsic to the cadmium atom. Moreover, it is in good agreement with the spin-orbit splitting of the Cd 4*d* level in free atom [23]. This doublet is identified by Freeouf as $d_{5/2}$ and $d_{3/2}$ bands to the CB transitions at X_6 lying at about 3.5 eV above the VB maximum. Considering Freeouf's results and our

data on $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$, both interpretations concerning the d maximum seem to be acceptable.

The last two features of reflectivity spectra are the h and i peaks appearing for host crystal at 18.8 and 21.4 eV respectively. The energy positions of both maxima shift linearly with the Fe content, although for higher concentration these maxima are undistinguishable.

The analysed influence of $\text{Fe}^{2+}(3d^6)$ states on the changes in energy positions of the reflectivity maxima confirms the existence of the empty Fe states in CB suggested by Kisiel et al. [16].

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