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REFLECTIVITY SPECTRA OF $\text{Cd}_{1-x}\text{Mn}_x\text{F}_2$ IN THE 5–35 eV ENERGY RANGE

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The reflectivity spectra of $\text{Cd}_{1-x}\text{Mn}_x\text{F}_2$ crystals, in the 5–35 eV energy range at 300 and 77 K, were investigated. The observed changes in the shape of spectra, caused by increase of the Mn content, are compared with the calculated band structure of pure CdF_2 and with the already available results of XPS experiments for these crystals. The increasing concentration of Mn results in the blurring of the reflectivity structures and shifts the energy of direct exciton (as compared to pure CdF_2). Qualitative arguments (hybridization of Mn^{2+} 3d and F^- 2p states) can describe these effects but a quantitative explanation would require a detailed band structure calculation for these compounds.

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The mixed crystals $\text{Cd}_{1-x}\text{Mn}_x\text{F}_2$, when $x \leq 0.1$, crystallize in the fluorite structure (cubic), in which Mn replaces Cd in the CdF_2 lattice. The lattice constant decreases linearly with the increasing concentration x of Mn, according to the Vegard's law [1]. In the CdF_2 band structure, the substitution of Cd with Mn atoms leads to several changes, which we examine by measuring the reflectivity spectra.

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The reflectivity measurements, in the 5–35 eV energy range, were performed at 300 and 77 K, using the synchrotron radiation facility PULS at the Frascati National Laboratories of INFN, Italy. The $\text{Cd}_{1-x}\text{Mn}_x\text{F}_2$ samples ($x = 0.0, 0.02$ and 0.1) were grown at the Institute of Physics, Polish Academy of Sciences, Warszawa, by the modified Bridgman method [2]. Our RT and LNT reflectivity spectra of pure CdF_2 are shown in Fig. 1. The spectra reveal several structures labelled as

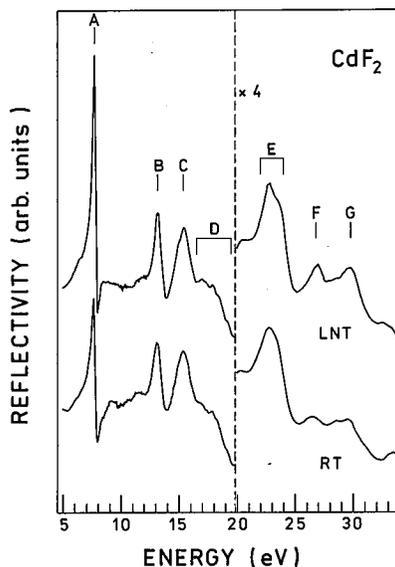


Fig. 1. The reflectivity spectra of pure CdF_2 at 300 K and 77 K. To distinguish the structure, the part of spectra from 20–35 eV was multiplied by the factor 4.

A, B, C, D, E, F, and G. The low temperature results show the distinguishable structure of *D* and *E* maxima, which we interpret on the basis of the calculated band structure. For the direct band gap, the value of 8.7 eV was assumed. The strong maximum *A* at 7.6 eV is attributed to the direct $1S$ exciton at Γ point. At low temperature the energy position of this peak shifts toward higher energies due to the negative temperature coefficient of the direct gap.

From the band structure calculated by Albert et al. [3] we can derive theoretical energy positions of all direct dipole allowed transitions at points of high symmetry in the Brillouin zone. A number of transitions at X and Γ points appears to be grouped in the energy range of the observed *B*, *C*, and *D* peaks. It is possible to isolate another group of transitions, responsible for the structured *E* peak.

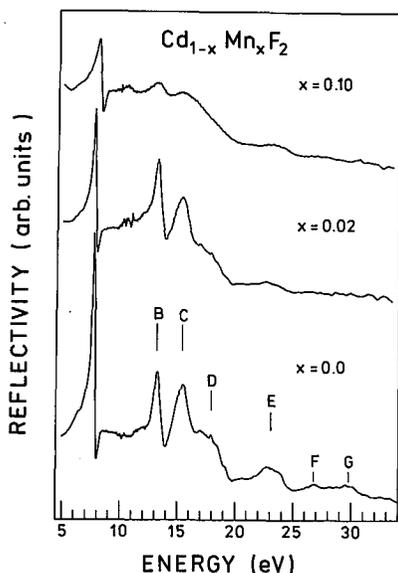


Fig. 2. The reflectivity spectra of mixed crystals $Cd_{1-x}Mn_xF_2$ at 300 K.

The reflectivity spectra of the mixed crystals are shown in Fig. 2. For Mn concentration $x = 0.02$, no marked changes are seen in the spectrum, aside from an overall decrease of the intensity of peaks. The energy positions of the maxima coincide, within our experimental resolution, with those of pure CdF_2 . This is also true for the A peak.

The major changes are observed for $x = 0.1$. The A maximum decreases in intensity and is shifted by 0.22 eV to higher energies. The structures B, C, and E are blurred and the D peak disappears. For the energy positions of the other maxima very small shifts are observed but without a definite trend in the direction.

To discuss the possible reasons for such a behaviour in the case of $Cd_{1-x}Mn_xF_2$, much help comes from the photoemission studies [4, 5]. It was found that the upper part of the valence band of $Cd_{1-x}Mn_xF_2$ crystals is mainly built from $Mn^{2+} 3d^5$ electrons, while the remaining part of the valence band retains the original $F^- 2p$ character. In this case one can assume that the density of 3d states, observed in the photoemission, originates from Mn $3d_{e_g}$ electrons which do not hybridize with $F^- 2p$ electrons. On the other hand, the Mn $3d_{t_{2g}}$ electrons hybridize with $F^- 2p$ valence band, modifying the initial states for optical transitions and, eventually, causing the blurring of the reflectivity spectra. In the case of the B, C, and D structures, the initial state for most of the eligible transitions originates from $F^- 2p$ electrons, so that in this region of the spectrum a stronger dependence upon manganese concentration is expected. At the same time, the presence of Mn $3d_{e_g}$ states at the top of the valence band can induce a lowering in energy of the $F^- 2p$

band due to $p-d$ repulsion. This fact can explain the change in energy position of the A peak.

In conclusion, the increasing concentration of Mn results in the blurring of reflectivity structures and shift in energy of the direct exciton, as compared to pure CdF_2 . Qualitative arguments can describe these effects but a quantitative explanation would require a detailed band structure calculation for the mixed crystal.

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