LIQUID NITROGEN AND ROOM TEMPERATURE REFLECTIVITY SPECTRA OF $Cd_{1-x}Fe_xSe$ IN THE 0.5-6.0 eV ENERGY RANGE

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The reflectivity measurements for mixed crystals $Cd_{1-x}Fe_xSe$ ($0.00 \leq x \leq 0.10$) have been carried out in an energy range of 0.5-6.0 eV at 300 and 77 K. The influence of $Fe^{2+}(3d^6)$ states on the changes in the energy positions of the reflectivity maxima E_0, $E_1(A_1)$, $E_1(A_2)$, and $E_1(B)$ is analyzed and the obtained results are consistent with the models existing in the literature.
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1. Introduction

The mixed crystals $Cd_{1-x}Fe_xSe$ belong to the group of materials known as "diluted magnetic semiconductors" (DMSs). These materials have been recently studied because of their important semiconducting as well as magnetic properties [1]. These ternary systems contain magnetic atoms, which randomly replace some of the cations in a II–VI semiconducting lattice. The intrinsic properties of Fe-based DMS have been studied using both the photoemission and reflectivity measurements and they are now resonably well understood. The predominant part of the physical properties of the DMS, in our case CdSe with Fe, depends on the location of the $Fe^{2+}(3d^6)$ states relative to the top of the valence bands (VBs) or bottom of the conduction bands (CBs).

The first reflectivity studies of the $Cd_{1-x}Fe_xSe$ have been carried out in the energy range of 4–10 eV by Kisiel et al. [2]. They discovered the linear shift of the maxima $E_1(A_2)$ and $E_1(B)$ with an increase in the Fe content. Taking into consideration the analyzed data of fundamental reflectivity measurements for CdFeSe and on the ground of photoemission results for CdMnTe, Kisiel et al. [2] presented one electron schematic diagram of the splitting and hybridization of $Fe^{2+}(3d^6)$ states in CdFeSe. On account of it, the $Fe^{2+}(3d^6)$ level splits into spin-up $d^5 \uparrow$ and spin-down $d^1 \downarrow$ states by the exchange interaction. Moreover,

these states, being in local tetrahedral structure, divide themselves into a doublet e and a triplet t_2 ones [3]. According to the local symmetry, the occupied t_2 states hybridize with p-like anion states, mainly giving the contribution to the top of VB. On the contrary the e states remain localized and one of them ($d^1\downarrow$) appears as a deep donor state close to the top of VB [2, 4]. Soon after, Taniguchi et al. [5] using their photoemission data suggested a slightly different model, in which e spin-down ($d^1\downarrow$) state was found at 0.5 eV below the top of VB. Very recently Sarem et al. [6] on the basis of existed models and their optical reflectivity studies on CdFeSe introduced a model of p–d hybridization for $A_{1-x}^{II}Fe_xB^{VI}$ wide-gap zinc-blende DMS, compared with the photoemission results of wurzite CdFeSe. They located the last spin-down ($d^1\downarrow$) state about 0.6 eV over the top of VB in agreement with the model of Kisiel et al. [2] and other experimental data (Ref. [4] and the references therein).

In this paper we present the reflectivity measurements made on the $Cd_{1-x}Fe_xSe$ ternary systems. The influence of the $Fe^{2+}(3d^6)$ states and their s–p–d hybridization with the bands of the host crystal allow one to explain the behaviour of the changes in shape and the energy positions of the fundamental maxima in reflectivity structure.

2. Experiment

The ternary system $Cd_{1-x}Fe_xSe$ crystallizes in the wurzite structure in the composition range $x \leq 0.20$ [6], where the Fe^{2+} ions randomly replace Cd^{2+} in the cation sublattice. Since FeSe crystallizes in the NiAs structure, the incompatibility of this crystal structure with the wurzite phase imposes an upper limit on x.

The reflectivity measurements of $Cd_{1-x}Fe_xSe$ crystals were carried out in the 0.5–6.0 eV energy range for two temperatures 300 K (RT) and 77 K (LNT). The monocrystalline samples of $Cd_{1-x}Fe_xSe$ ($x = 0.0, 0.05, 0.10$) used in these studies were prepared in the Polish Academy of Sciences (Warsaw), by the modified Bridgman method using the individual elements as the starting materials. The samples were cleaved perpendicularly to c-axis. The measurements have been performed using conventional unpolarized light, therefore as the result we obtained the structure with the main contribution coming from $E \perp c$ polarization as well as small contribution from $E \parallel c$ one. The lattice constant was determined at room temperature by X-ray powder diffraction, using Debye–Scherrer method. The linear dependence on the lattice constant $a(x)$ as the function of concentration x is shown in Fig. 1. The dependence $c(x) = 1.63a(x)$ is in good agreement with the data existing in literature [7]. The samples were polished and etched in 2% bromine solution in methyl alcohol and afterwards cleaned with methyl alcohol just before the experiment.

The measurement procedures and experimental apparatus are described elsewhere [8, 9]. This method has a resolving power better than 0.01 eV. It is worth mentioning that the reflectivity spectra deliver indirect information on joint density of states (JDOS) because the absorption mechanism for this technique, governed by van Hove singularities, is related only to the energy intervals between VBs and CBs [10].
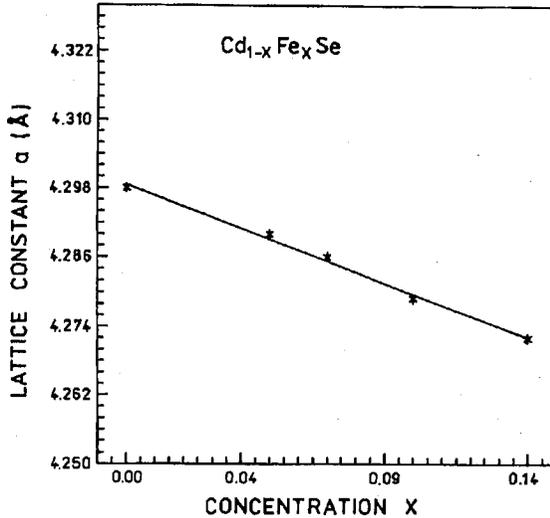
Fig. 1. The dependence of the lattice constant on the Fe concentration $a(x)$.

3. Results and discussion

The reflectivity spectra of $Cd_{1-x}Fe_xSe$ at RT and LNT are shown in Fig. 2a and 2b, respectively. The structure of the reflectivity spectra of cadmium selenide with iron is compared with that of the host crystal, the pure CdSe. The main maxima named as E_0, $E_1(A_1)$, $E_1(A_2)$, $E_1(B)$ are marked by arrows. As one can see, with increasing Fe concentration, there are some changes in shapes and energy positions of the maxima, and also their reciprocal intensities. For the Fe concentration used in our investigation (up to $x = 0.10$) the structures are much more blurred as it was in the case of cadmium telluride with iron [11]. Only the peak E_0 is well pronounced, the maxima E_1 are weakly visible, however Sarem et al. [6] as well as Kowalski et al. [12] in their papers do not notice these significant structures of E_1 maximum resulting from the splitting of the bands because of spin–orbit (S–O) interaction. The first maximum E_0 on the CdSe curve is associated with the transition at Γ point between the top of VB (Γ_6) and the bottom of CB (Γ_1), which suits the energy gap E_g. Looking over the reflectivity spectra $Cd_{1-x}Fe_xSe$ — see Fig. 2a and 2b and data presented in Table, one can notice that the maximum E_0, related to E_g, shifts towards higher energy and its energy position is the linear function of Fe content according to the following equations:

RT $E_0(x) = 0.76x + 1.73,$

LNT $E_0(x) = 0.86x + 1.76,$

at room and liquid nitrogen temperature, respectively.

The maximum E_1 in the zinc-blende structure results from the transitions between the bands along Λ direction. In the case of wurzite structure this maximum is split into A and B components. The S–O interaction causes the splitting of A component into A_1 and A_2 allowed only for $E \perp c$ polarization which are well
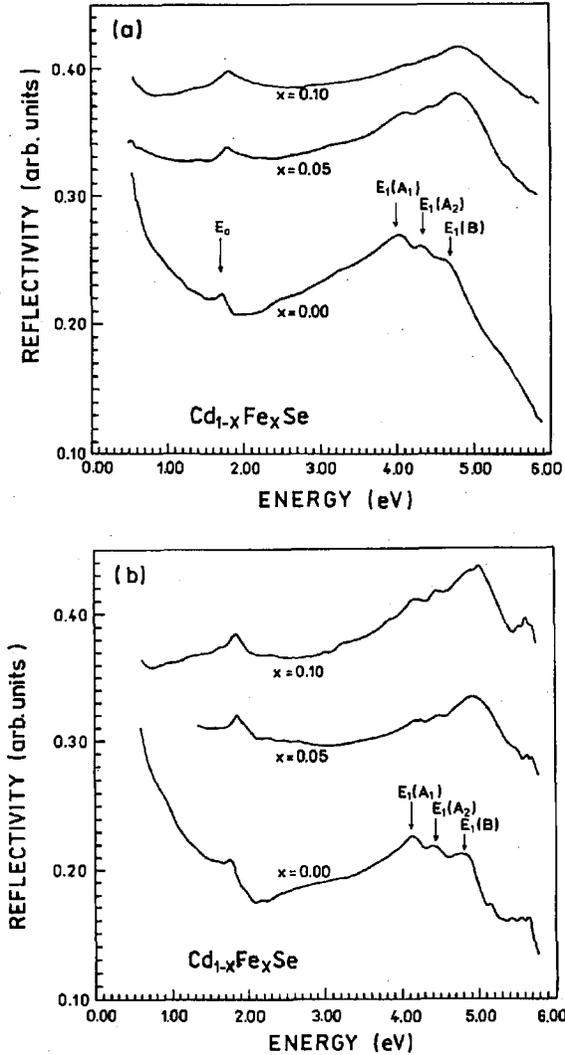
Fig. 2.   The reflectivity spectra of $Cd_{1-x}Fe_xSe$ in the 0.5–6.0 eV energy range at: (a) room temperature (RT) and (b) liquid nitrogen temperature (LNT).

observed in our spectra. Maximum $E_1(B)$ appears at the same energy position for both types of polarization. The origin of these maxima $E_1(A)$ and $E_1(B)$ is explained in different way by different authors [13–15]. According to Bergstresser and Cohen [13] maxima $E_1(A_1)$ and $E_1(A_2)$ are due to the transitions at Γ point in contrary to Cardona and Harbeke [14] who associate these maxima with the transitions along the Δ direction, but in both cases the appearance of these two maxima results from S–O interaction. Our experimental data (see Table) show the linear dependences $E_1(A_1)$ and $E_1(A_2)$ energy positions on the Fe content with

TABLE

The energy positions of the maxima in the reflectivity spectra of $Cd_{1-x}Fe_xSe$.

Maximum Name	$x = 0.00$		$x = 0.05$		$x = 0.10$	
	RT	LNT	RT	LNT	RT	LNT
E_0	1.72	1.76	1.78	1.80	1.80	1.85
$E_1(A_1)$	4.03	4.14	4.12	4.25	4.17	4.18
$E_1(A_2)$	4.31	4.42	4.40	4.51	4.43	4.46
$E_1(B)$	4.70	4.85	4.76	4.94	4.79	5.01

the same slope in room as well as in liquid nitrogen temperature

RT $E_1(A_1)(x) = a_1 x + 4.04;$ $a_1 = 1.4 \pm 0.2$ [eV]$/x$,

$E_1(A_2)(x) = a_2 x + 4.32;$ $a_2 = 1.2 \pm 0.2$ [eV]$/x$,

LNT $E_1(A_1)(x) = a_1 x + 4.17;$ $a_1 = 0.4 \pm 0.2$ [eV]$/x$,

$E_1(A_2)(x) = a_2 x + 4.44;$ $a_2 = 0.4 \pm 0.2$ [eV]$/x$.

It seems to us that our results confirm the splitting of initial states of the discussed maxima. The energy positions of $E_1(B)$ maxima are also the linear function of Fe concentration at RT and LNT. The behaviour of the reflectivity features shows that with the increasing Fe content the energy intervals for considered transitions become larger. It can be consistently explained if one assumes that the substitution of Cd ions by Fe ones gives the access to pushing upwards the bottom of conduction bands what causes the distance between VB and CB to be larger. Similar mechanism should also work at other high symmetry points in Brillouin zone (BZ). Since the reflectivity measurements show only the interband transitions we cannot state anything about the existance of the deep donor state localized in the energy gap [24]. Taking into account the model mentioned above one can expect the influence of hybridization of $Fe(3d^6)$ states with p-like anion states in the valence bands. It could lead to broadening and blurring of the reflectivity structure mainly for the transitions occurring at Γ point at BZ. Hence it could explain relatively big smearing of $E_1(A)$ maxima and the change of their reciprocal intensities in comparison with $E_1(B)$ maximum.

Therefore, we can assume that the interaction in the VB region between d states of Fe and especially p-like states of Se as well as a possible movement of the lowest CB, may influence the transitions near Γ point what is manifested by E_1 energy positions dependence of the Fe concentration.

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