Cd$_{1-x}$Fe$_x$Se room-temperature reflectivity in the 10-25 eV energy range

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Abstract. The reflectivity spectra of Cd$_{1-x}$Fe$_x$Se ($x = 0$, 0.07 and 0.14) have been measured in the energy range 10–25 eV and structures have been assigned to transitions from the Cd 4d and Se 5s states to the conduction bands. The assignment has been supported by theoretical *ab-initio* calculations of the band structure and the optical properties of pure hypothetical zincblende CdSe. The band structure and the density of states have been obtained using the self-consistent relativistic LMTO method. The theoretical spectrum has been calculated with the inclusion of k-dependent transition matrix elements. The energy shifts of the maxima as the Fe concentration increases have been discussed.

1. Introduction

In recent years a new class of II–VI diluted magnetic semiconductors (DMS), in which the group II element has been randomly replaced with Fe^{2+}, has become the focus of intense research activity. Unlike the very well known Mn-based DMSs [1], the iron-based II–VI compounds have a very low solubility of Fe, and this creates some difficulties in obtaining optically good samples.

Cd$_{1-x}$Fe$_x$Se crystallizes in the wurtzite structure for $x \leqslant 0.15$ [2] but, even for such a small amount of Fe, the changes in the fundamental reflectivity spectra caused by the presence of iron are noticeable [3–5]. The substitution of Cd with Fe atoms causes several effects on the band structure of pure CdSe. In the low-concentration limit, the Fe ions can be regarded as impurities. Let us focus on the Fe 3d states. In the high-spin configuration, these states are split by the exchange interaction into well separated spin-up (3d↑) and spin-down (3d↓) levels, each of which is further split by the crystalline field. In the zincblende II–VI semiconductors the crystalline field around the transition-metal atoms has tetrahedral symmetry. In the wurtzite structure—the structure into which CdSe crystallizes—because of a slight distortion along the ⟨111⟩ direction, the local symmetry around the magnetic ions becomes trigonal (C$_{3v}$ point group). Symmetry arguments show that each of the two spin-up and spin-down groups of d states is split into a doublet e (d$_{xy}$, d$_{x^2-y^2}$), a singlet a (d$_{z^2}$) and a doublet e (d$_{yz}$, d$_{zx}$). However in the literature [3, 4, 7] the distortion is neglected

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and the local symmetry of the crystal field is usually taken to be tetrahedral (T_d). In this field the d states are split into a doublet e ($d_{x^2-y^2}$, d_{z^2}) at low energy and a triplet t_2 (d_{xy}, d_{yz}, d_{zx}) at high energy. Within the tetrahedral approximation, the six 3d electrons of the Fe^{2+} ion fill the five 3d spin-up states and one of the e spin-down states. The latter seems to act as a deep donor state, placed in the energy gap at about 0.6 eV above the top of the valence bands [6, 7].

In a first attempt to describe the Fe 3d states in $Cd_{1-x}Fe_xSe$, Kisiel *et al* [3] considered the $3d^1$ e↓ state as a localized state lying about 0.6 eV above the top of the valence bands, as suggested by previous workers [6, 7], while the t_2↑ states hybridize with the highest valence bands derived mostly from the Se 5p states and the filled e↑ lies below them as a localized state. Instead, from resonant photoemission studies, Taniguchi *et al* [8] reached the conclusion that in $Cd_{0.6}Fe_{0.4}Se$ the $3d^1$ e↓ and $3d^2$ e↑ states show up in the photoemission spectra as narrow peaks at 0.5 eV and 3.7 eV, respectively, below the valence band maximum. In agreement with Kisiel *et al* [3], Taniguchi *et al* [8] considered that the filled t_2↑ states hybridized with valence bands. More recently, Sarem *et al* [4] suggested that a model similar to those working for wide-gap zincblende DMSs should hold also for $Cd_{1-x}Fe_xSe$. They suggested also the existence of empty Fe 3d states in $Cd_{1-x}Fe_xSe$ between the lowest and the second-lowest group of conduction bands.

Direct information on the empty states of $Cd_{1-x}Fe_xSe$ is not yet available. For this reason we measured the reflectivity of $Cd_{1-x}Fe_xSe$ ($x = 0$, 0.07, and 0.14) between 10 and 25 eV, where the almost dispersionless Se 4s and Cd 3d states are excited. We found that the energies of the reflectivity maxima shift with increasing Fe content and we related those shifts to modifications of the conduction bands introduced by the presence of Fe.

Section 2 provides the experimental details. The discussion and interpretation of the reflectivity spectra supported by *ab-initio* calculations of pure hypothetical zincblende CdSe are presented in section 3. In section 4 we draw the conclusions.

2. Experiment

The reflectivity measurements of $Cd_{1-x}Fe_xSe$ ($x = 0$, 0.07 and 0.14) were performed at room temperature using the vacuum-ultraviolet beam line of the PULS synchrotron radiation facility in Frascati. The radiation emitted by the electrons accelerated in the ADONE storage ring is focused onto the entrance slit of a modified 1 m normal incidence Hilger & Watts monochromator. The average resolution of the set-up was 0.1–0.2 nm over the entire energy range [9].

The samples used in the present study were grown by means of a modified Bridgman method at the Institute of Physics, Polish Academy of Sciences, Warsaw. The nominal Fe content was checked by x-ray diffraction measurements of the lattice constants a and c, using the dependences $a(x)$ and $c(x)$ [10], where x is the concentration of Fe. Before being inserted inside the vacuum chamber of the reflectometer, the samples were washed in methyl alcohol and attached to the sample holder with the c axis perpendicular to the sample surfaces. The reflectivity was measured at near-normal incidence, in which case the radiation electric field E is almost perpendicular to the c axis. Therefore we obtain the reflectivity spectra mainly for $c \perp E$ polarization with some addition of structures occurring for $c \parallel E$ polarization [3]. The surfaces of the samples containing Fe appear to be inhomogeneous, as a mosaic of small grains with slightly different orientations and with many scratches along the surface, indicating the presence of severe stresses inside the samples. The reflectivity spectra were slightly affected by the scattered radiation.

3. Results and discussion

Figure 1 shows the reflectivity spectra of $Cd_{1-x}Fe_xSe$ in the energy range 10–25 eV. The main features are named in the notation introduced for CdTe and ZnTe [9]. The values of the energy positions of the reflectivity structures are listed in table 1. Generally, the presence of the Fe ions in CdSe leads to some changes in the relative intensities of the reflectivity structures as well as to shifts in the energy positions of the reflectivity maxima towards higher energies.
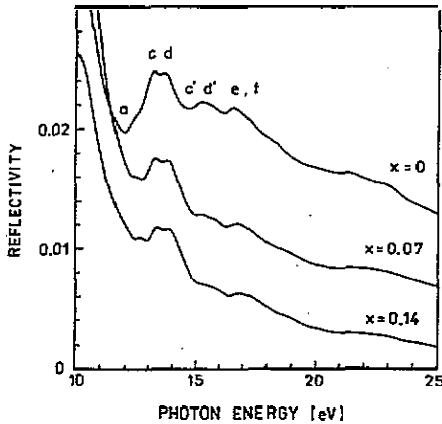

Figure 1. The reflectivity spectra of $Cd_{1-x}Fe_xSe$ for different Fe concentrations x. The spectra corresponding to the values of $x = 0$ and $x = 0.07$ have been shifted upwards by 0.01 and 0.005, respectively.

Table 1. Energies of the structures observed in the reflectivity spectra of $Cd_{1-x}Fe_xSe$ between 10 and 25 eV. The last column gives the slope of the (linear) shift of the maxima due to the increase in Fe.

	Energy (eV)			
Maximum	$x = 0$	$x = 0.07$	$x = 0.14$	$\Delta E/\Delta x$ (eV)
a	12.35 ± 0.05	12.50 ± 0.05	12.65 ± 0.05	2.1 ± 0.5
c	13.15 ± 0.05	13.25 ± 0.05	13.35 ± 0.05	1.4 ± 0.5
d	13.60 ± 0.05	13.78 ± 0.05	13.82 ± 0.05	1.6 ± 0.5
c', d'	15.20 ± 0.10	15.27 ± 0.1	15.30 ± 0.1	0.7 ± 1.0
e, f	16.55 ± 0.05	16.73 ± 0.05	16.85 ± 0.05	2.1 ± 0.5

3.1. CdSe: interpretation of experimental data

The reflectivity spectrum of pure wurtzite CdSe is in very good agreement with that measured by Freeouf [11], who did not find a significant change due to polarization in the 10–25 eV energy region. The interpretation of the reflectivity structures for CdSe is more difficult with respect to the zincblende semiconductors such as CdTe and ZnTe, since the reduced symmetry of the crystal structure increases the number of empty conduction bands. The spectrum of the effective number of electrons participating in optical transitions, calculated by Freeouf [11] up to 25 eV for CdSe, shows a tendency to saturate before starting a second steep increase. The limiting value of the saturation can be extrapolated to six or seven electrons per molecule. This suggests that the oscillator strength for the valence band

transitions is almost exhausted above 10 eV. In addition, lifetime broadening associated with valence-to-conduction band transitions, which increases with increasing energy of the excited electron, becomes large enough to smear out the ϵ_2 structures, as shown in the next section. For these reasons, following Freeouf [11] and from the theoretical calculations presented below, we think that most of the reflectivity structures observed above 10 eV should be assigned to the excitation of the Cd 4d and the Se 4s electrons.

In CdSe the Cd $4d_{5/2}$ level lies 9.8 ± 0.1 eV below the top of the valence bands [12, 13]. The binding energy of the Se 4s level is not well determined, since in the photoemission spectra a structure associated with these levels has not been identified. Shevchik *et al* [14] suggested a binding energy of 11.7 eV for the Se 4s bands, in good agreement with the value of 11.1 eV calculated by Kobayashi *et al* [15] using the semi-empirical tight-binding method, and with the value of 12.4 eV found by us for zincblende CdSe. Adding the fundamental energy gap (1.8 eV at room temperature [4, 5, 16]) of CdSe to the binding energy of the core levels, we place the thresholds for the transitions originating in the Cd $4d_{5/2}$ states and the Se 4s state at 11.6 ± 0.1 eV and 13.5 ± 0.1 eV, respectively. From an inspection of the calculated energy bands of wurtzite CdSe [15, 17], one can infer that the conduction band density of states is smooth and very small near the bottom of the conduction bands. In addition, the Cd 5s character of these bands should make the transition matrix elements from the Cd 4d and the Se 4s states very weak. For these reasons, confirmed by the ϵ_2 calculations performed for the zincblende CdSe, we do not assign any reflectivity structure to these thresholds, as we already suggested for other II–VI compounds [9].

Let us begin the discussion by considering transitions from the Cd 4d states, which should yield the Cd p-like projected density of conduction states.

The two peaks labelled in figure 1 as c and d, occurring for pure CdSe at 13.15 eV and 13.60 eV, respectively, form the first significant structure present in the core-level reflectivity spectrum. Their separation of 0.45 eV is smaller than the Cd $4d_{5/2}$–$4d_{3/2}$ spin–orbit splitting (0.7 eV) determined in photoemission experiments [14]. It is possible that they correspond to a spin–orbit doublet from the Cd $4d_{5/2}$–$4d_{3/2}$ states to Cd p-like conduction states located approximately 1.55 eV above the bottom of the conduction bands, as suggested by Freeouf [11]. From the energy band calculations of Bergstresser and Cohen [17], we suggest that states along or around the Γ_3–Δ–$A_{1,3}$ direction are possible final states for these two maxima. In support of this assignment we note that the $E_1(A_1)$ peak at 4.13 eV [11] in the fundamental reflectivity spectrum is assigned to the Γ_{5v}–Γ_3 transition, i.e. it has almost the same final states as feature c. We can thus write the following relation: energy of peak c = (energy of $E_1(A_1)$ − (separation Γ_{3v}–Γ_{6v}) + (binding energy of Cd $4d_{5/2}$) = $(4.18 - 0.6 + 9.8)$ eV = 13.3 eV, in very good agreement with the energy measured for the maximum c in the Cd 4d core reflectivity spectrum of CdSe. Looking at the calculated band structure of CdSe [17], another region of high density of Cd p-like states could be located along the $L_{1,3}$–U–M_3 direction, showing a minimum along the U direction. The calculated energy separation between the Γ_{3c}–$\Gamma_{1,3c}$ states is 0.7 eV, a little higher than the experimental separation of peaks c and d. This coincidence suggests that probably peak d is composite, being derived from both groups of transitions. It is well known that there should be a close correspondence between the reflectivity structures of zincblende compounds and wurtzite compounds of the same family [17]. In CdTe, peaks c and d, separated by 0.45 eV, have been assigned by Kisiel *et al* [9] to final states around X_6 (maximum c) and to the first peak of the conduction band density of states (maximum d). Previous calculations performed for zincblende structures (CdTe, ZnTe and HgTe) [18] show that also the L_1 state contributes to the structure of the calculated ϵ_2. The Λ direction of the zincblende Brillouin zone can be mapped on the unfolded Λ

direction in the wurtzite Brillouin zone, the L$_1$ point becoming the Γ_3 state. Similarly, the region around the cubic X point becomes the L–U–M direction in the wurtzite structure. This gives the correspondence between the c–d features of the reflectivities of CdTe and CdSe.

After a region of low density of states approximately 1.5 eV wide and centred at about 3.5 eV above the bottom of the conduction bands, the calculated band structures show again the possibility of a strong p-like density of states between 5.5 and 7 eV, centred around the Γ_6, Γ_1 and Γ_5 states and the K$_3$ state [17]. These states correspond to the Γ_{15} and the L$_{6c}$ states in the zincblende Brillouin zone, which have been assigned to the final states for the e and f structures of the reflectivities of CdTe and ZnTe [9]. We assign the broad structure of the CdSe reflectivity found at 16.55 eV, labelled in figure 1 as e, f, approximately 5 eV above the Cd 4d$_{5/2}$ threshold, to the transitions from the Cd 4d$_{5/2}$ core level to the second-lowest group of conduction bands. According to this assignment, the calculated bands seem a little too high with respect to the conduction band minimum.

Generally the oscillator strength for transitions starting from d states is higher than that for transitions starting from s states. In addition, the conduction bands should have little Se character and the lifetime broadening of the Se 4s states should be larger than that for the Cd 4d states. All these arguments suggest that the transitions from the Se 4s states should be weaker and broader than those derived from the Cd 4d states; so they should give unimportant features. In fact, UV photoemission spectra do not show structures corresponding to the Se 4s levels. However, the CdSe reflectivity spectrum shows a broad feature c', d' at 15.2 eV, approximately 3.2 eV above the Cd 4d threshold, just where the conduction band density of sates [17] should present a minimum, as discussed above. This region with a low density of states also affects the fundamental reflectivity spectrum of CdSe, being responsible for the dip at 6 eV [17]. We suggest that the c', d' reflectivity maximum could be assigned to transitions originating in the Se 4s states, with the same final states as peaks c and d. The average separation between the c', d' structure and peaks c and d is 1.8–2.0 eV, in very good agreement with the estimated separation between the Cd 4d$_{5/2}$ state and the Se 4s state. This interpretation is strongly supported by the ϵ_2 calculations of zincblende CdSe presented in the next section.

The shoulder a on the low-energy side of the reflectivity maximum c does not correspond to structures of the conduction band density of states even for the zincblende compounds CdTe and ZnTe. There has been some controversy on the interpretation of this feature regarding whether to assign it to band-to-band transitions [19] or to a core exciton associated with the Cd 4d$_{5/2}$ states [9]. At present the latter interpretation has been accepted and we interpret the shoulder a as a core Cd 4d$_{5/2}$ exciton, resonant with the conduction band continuum, bound to a higher-energy conduction band minimum.

3.2. CdSe: theoretical calculations for the hypothetical zincblende structure

Cadmium selenide crystallizes in the wurtzite structure (space group, C$_{6v}^4$) which is closely related to the zincblende structure (space group, T$_d^2$) [20]. The hexagonal wurtzite crystal has a unique crystallographic axis of symmetry, namely the c axis, which corresponds to the $\langle 111 \rangle$ axis of the cubic zincblende structure. If we compare the cubic band structure with the hexagonal structure, we can see a one-to-one correspondence between states along the Λ (cubic) and states along the Δ (hexagonal) symmetry line going from Γ to A and back to Γ. So the Λ direction in the zincblende structure is quite similar to the 'unfolded Δ direction' in wurtzite [17]. The similarity of the optical spectra at high energies between wurtzite and zincblende found for instance in ZnS, which crystallizes in both structures, suggests that the similarity of these materials goes beyond the Λ–Δ correspondence.

We have calculated the bands of CdSe in the zincblende structure. Our choice is supported not only by similarities of these structures but also by the fact that, for the energy region under consideration (i.e. above 10 eV), Freeouf [11] did not see any polarization dependence in the optical spectrum. The bond length (i.e. the nearest cation–anion distance) was assumed to be the same in both structures. For hypothetical cubic CdSe the lattice parameter a_{zb} is equal to 6.081 Å which is related to the hexagonal CdSe lattice parameter $a_w = 4.3$ Å according to the simple formula $a_{zb} = \sqrt{2a_w}$.

The band structure and the density of states of CdSe have been obtained using the conventional *ab-initio* self-consistent relativistic LMTO method [21, 22]. The exchange–correlation local-spin-density approximation potential was used in the form proposed by Vosko *et al* [23]. The crystal was considered as an FCC lattice with four sites in the basis, Cd(0, 0, 0), Se($\frac{1}{4},\frac{1}{4},\frac{1}{4}$), E1($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) and E2($\frac{3}{4},\frac{3}{4},\frac{3}{4}$), where E1 and E2 stand for 'empty spheres' [24]. Scalar relativistic corrections (i.e. Darwin shift and mass velocity) as well as the 'combined correction term' [21, 22] were consistently applied in the self-consistent procedure. In the final band-structure calculation the spin–orbit coupling was included as a formal perturbation term in the Hamiltonian [21]. The energy eigenvalues and wavefunctions were used to determine the complex dielectric function. All calculations were carried out in a single energy panel, using 4s, 4p and 4d basis functions for Se and 5s, 5p and 4d functions for Cd. The total number of bands is equal to 36, the first nine of them being situated below the Fermi energy.

The self-consistent band structure of hypothetical zincblende CdSe is presented in figure 2. The total density of states is shown in figure 3.
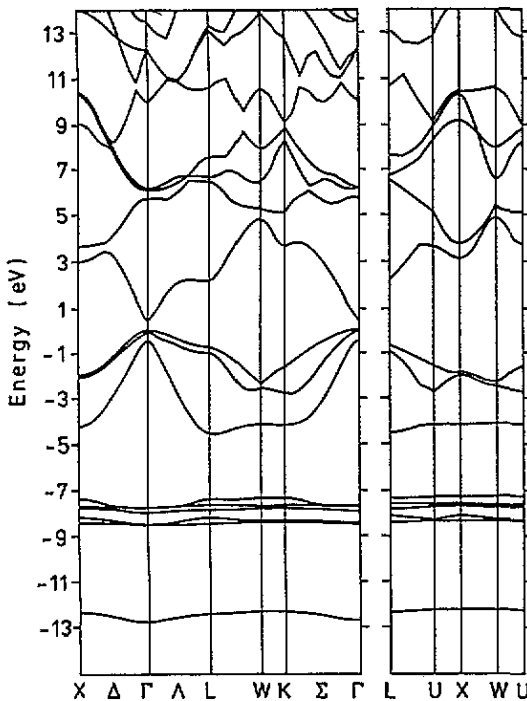

Figure 2. The calculated band structure of CdSe in the zincblende symmetry.

The optical absorption is proportional to the imaginary part of the dielectric function. In the limit of vanishing linewidth, the contribution of the interband transitions to the imaginary

part $\epsilon_2(\omega)$ of the dielectric function is given by the following expression [25]:

$$\epsilon_2(\omega) = \frac{1}{\omega^2} \sum_f \sum_i \int_{BZ} |M_{fi}^k|^2 \delta(E_f^k - E_i^k - \hbar\omega)\, dk \tag{1}$$

where E_i^k and E_f^k are eigenvalues of the occupied and empty states, respectively, at a given k-vector; $M_{fi}^k = \langle fk|p|ik\rangle$ is the dipole matrix element of the momentum operator $p = -i\hbar\nabla$.

In the full band calculations that provide both eigenvalues and eigenfunctions, it is possible to compute the matrix elements at all considered k-points [26]. The theoretical spectrum was obtained with the inclusion of k-dependent transition matrix elements. The integration of equation (1) over k-space was performed by the tetrahedron method [27] based on 240 k-points in the irreducible part of the Brillouin zone.

It is found experimentally that the initial and final states have finite lifetimes [28]. The effects of the finite relaxation time imply a Lorentzian line shape of the initial and final states which manifests itself as a broadening of the spectrum. This effect was incorporated in our single-particle results by convoluting the spectrum with a Lorentzian function the width of which depends on the final-state energy (Γ_L increases significantly with increasing energy of the final state [28]):

$$\bar{\epsilon}_2(E) = \frac{1}{2\pi} \int \frac{\epsilon_2(E')\Gamma_L(E')}{(E' - E)^2 + \Gamma_L(E')^2/4}\, dE' \tag{2}$$

where $\Gamma_L = \Gamma_0 + 0.1(E_f - E_F)$; Γ_0 stands for the Lorentzian FWHM of the core levels; E_f and E_F denote the final energy and Fermi levels, respectively. $\Gamma_0 = 0.42$ eV for Se 4s and 0.22 eV for Cd 4d states [29].

The imaginary part $\bar{\epsilon}_2(\omega)$ of the dielectric function with lifetime broadening included is shown in figure 4. There are four curves displayed in the figure. The broken curve represents the contribution to the imaginary part $\bar{\epsilon}_2(\omega)$ which results from the transitions from the first band (Se 4s states) to the bands lying above the Fermi level. The contribution originating from bands 2–6 (Cd 4d states) is represented by the chain curve. The dotted curve describes the transitions from bands 7–9 (valance bands). Finally, the total imaginary part $\bar{\epsilon}_2(\omega)$ of the dielectric function is represented by the full curve. The calculated $\bar{\epsilon}_2(\omega)$ curve (full curve) presented in figure 4 reproduces very well the main structures and the energies of the CdSe reflectivity spectrum in the 10–20 eV energy range shown in figure 1.

The theoretical binding energies of Se 4s states (12.4 eV) and Cd 4d states (7.8 eV) do not agree with the experimental values [12, 14]. The discrepancy between the observed and calculated binding energies of the Se 4s and Cd 4d states is a correlation effect, which is mainly the result of the change in the occupancy of the core levels in the excitation process. The binding energies were corrected following the procedure described in [26].

Careful analysis of the contribution to the imaginary part $\bar{\epsilon}_2(\omega)$ originating from different core levels as well as regions in the Brillouin zone giving the most significant contribution to the reflectivity structures in the energy range 10–20 eV, lead to the following conclusions.

(1) The two maxima labelled c and d are assigned to transitions originating in the Cd 4d states, with final states in the region not only around the X point but also the K and U points in the zincblende Brillouin zone. We should keep in mind the mapping of the cubic X point on the L–U–M direction and the K and U points on the Γ–Σ–M direction in the wurtzite structure. Therefore on the basis of the zincblende calculations we suggest that structures c
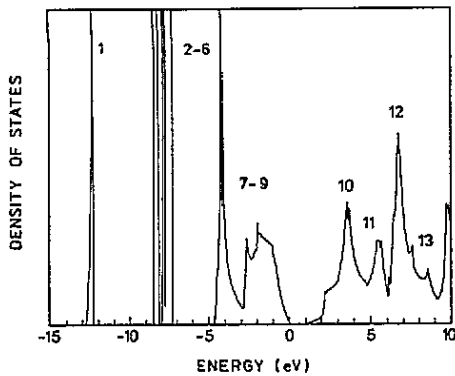
Figure 3. Total density of states of CdSe. The numbers near the main peaks in the figure denote the serial numbers of the bands.
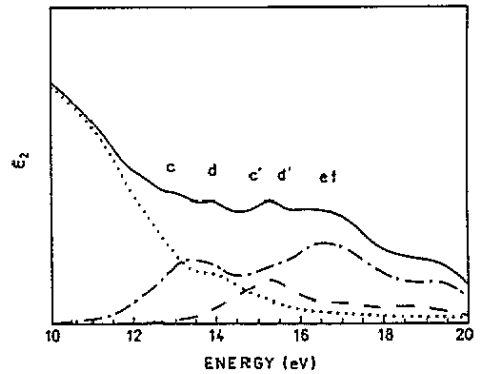
Figure 4. Imaginary part $\bar\varepsilon_2(\omega)$ of the dielectric function of hypothetical zincblende CdSe (——): – – –, contribution from the transitions from the Se 4s states; — · —, contribution from the transitions originating from the Cd 4d states; · · · · · ·, contribution from the transitions from the valence bands.

and d are described by transitions to final states lying along the $L_{1,3}$–U–M_3 and Γ_3–Σ–M_1 directions.

(2) The feature c′, d′ in the zincblende CdSe imaginary part of the dielectric function originates from excitations of electrons from the Se 4s bands to final states at X, K and U points in the zincblende Brillouin zone. This means that the final states lie along the $L_{1,3}$–U–M_3 and Γ_3–Σ–M_1 directions in the wurtzite Brillouin zone. So the c′, d′ reflectivity maximum is assigned to transitions to the same final states as in the case of the maxima c and d.

(3) The structure e, f has been assigned to transitions from Cd 4d states to conduction bands around the Γ and L points in the zincblende Brillouin zone. Taking into account the direct correspondence between the Γ and L directions in the zincblende structure and Γ–A–Γ in the wurtzite structure, we assign these final states as Γ_6, Γ_1 and Γ_5 in the wurtzite Brillouin zone.

3.3. $Cd_{1-x}Fe_xSe$: interpretation of experimental data

The $Cd_{1-x}Fe_xSe$ core level reflectivities presented in figure 1 show marked changes as was the case for the fundamental reflectivity measured in the energy range from 4 to 10 eV [3].

The binding energy of the core levels, referred to the valence band maximum, remains the same upon alloying CdTe with Mn, as measured by photoemission [30]. In the case of $Cd_{1-x}Fe_xSe$ the situation is more complicated, since the Fe 3d $e{\downarrow}$ states lie above the Se 4p valence band maximum [3, 8, 12, 31]. If we continue to use the latter as the reference energy, the Cd 4d binding energy also does not change for $Cd_{1-x}Fe_xSe$ [12]. Thus the variation in the energies of the core reflectivity maxima must be related to the shifts in the conduction band states with respect to the top of the valence bands.

Two major effects may cause these shifts. First, by substituting Cd atoms with Fe atoms, the Cd 5s and 5p states are replaced by the Fe 4s and 4p states, which have a lower binding energy. This will push the conduction bands upwards. Indeed, the increase in the fundamental energy gap of the Mn-based DMS is attributed to such an effect [1]. The Fe empty states lie closer to the Cd empty states than the Mn states do, and thus a smaller

shift in the conduction bands is expected. A change in the conduction band shape is related to the addition of the Fe 3d empty states, which should be of t_2 symmetry and thus should have an influence on p-like states with the same symmetry.

The maxima c and d of the pure CdSe reflectivity spectrum shift towards higher energies while the Fe concentration increases. The slope of the linear shift of these structures is $(1.4–1.6) \pm 0.5$ eV/x. This value is in perfect agreement with the slope of the low-energy $E_1(A_1)$ maximum [3, 16]. The agreement between the two energy variations with iron concentration suggests that for the $E_1(A_1)$ maximum the shift is mostly due to a final-state effect, and that the Γ_{6v}–Γ_{5v} splitting is only slightly affected by the increase in Fe alloying.

When iron is added to CdSe, the energy of the e, f reflectivity structure increases, following the relation $E_{e,f} = 16.55 + (2.1 \pm 0.5)x$ eV. The value of the slope in this case can be related to that of the low-energy E_2 maximum at 7.1 eV [3]. This maximum was assigned to transitions occurring at or around the K symmetry point of the zincblende Brillouin zone. If we assume that the final states of the e, f structure and those of the E_2 maximum are the same, we can again deduce a very small effect of Fe on the energy of the uppermost valence bands.

The behaviour of the reflectivity structures of Cd$_{1-x}$Fe$_x$Se differs from those of Cd$_{1-x}$Fe$_x$Te and Cd$_{1-x}$Mn$_x$Te mixed semiconductors. In fact, in the latter cases the reflectivity maxima associated with the Cd 4d core states did not shift signifiantly upon alloying with the transition metal. Instead a variation in the shape of the spectra was noticed. In particular, in Cd$_{1-x}$Mn$_x$Te the dip at 15 eV present in pure CdTe has been filled up with increasing Mn, indicating the build-up of a conduction band at about 4.5 eV above the valence bands, derived from the Mn 3d empty states [32]. In the present case we found a shift in the energy peaks which we related to a shift in the empty conduction bands. In particular, the variation in the e, f structure is larger than that of structures c and d, indicating a stronger influence of Fe on the second group of conduction bands than on the lowest group. In the absence of detailed calculations we can speculate that the larger shift of the second group of conduction bands is in part determined by repulsion between the Cd p-like final states and the Fe 3d $t_2\downarrow$ empty level. The existence of this level between the two groups of conduction bands has been suggested by Sarem *et al* [4] from the analysis of the fundamental reflectivity spectra.

4. Conclusions

The reflectivity spectra of Cd$_{1-x}$Fe$_x$Se ($x = 0$, 0.07 and 0.14) have been measured in the energy range 10–25 eV and the structures have been assigned to transitions from the Cd 4d and Se 5s states to the conduction bands. The assignment has been supported by theoretical *ab-initio* calculations of the band structure and optical properties of pure hypothetical zincblende CdSe. The band structure and density of states have been obtained using the self-consistent relativistic LMTO method. The theoretical ϵ_2 spectrum has been calculated with the inclusion of k-dependent transition matrix elements.

The shoulder a is not present in the one-electron calculations and we interpret it as a core exciton associated with Cd 4d$_{5/2}$ states.

The two peaks labelled c and d are described as transitions from the spin–orbit split Cd 4d$_{5/2}$–4d$_{3/2}$ initial bands to final states lying around Γ_3–Δ–A$_{1,3}$ states in the Brillouin zone. The maximum d also has a significant contribution which is derived from transitions to final states located along the L$_{13}$–U–M$_3$ direction.

We assign the broad feature c′, d′ in the CdSe reflectivity spectrum to transitions from Se 4s states to final states along the L$_{13}$–U–M$_3$ direction.

The Γ_6, Γ_1 and Γ_5 states are assumed to be the final states for structure e, f, for which the initial states lie in the Cd 4d levels.

The presence of the Fe ions in CdSe leads to some changes in the relative intensities of the reflectivity structures. Shifts in the maxima towards higher energies appear. We suggest that the upper valence bands are only weakly affected by the increase in iron concentration, unlike the conduction bands, which shift to higher energies.

Acknowledgments

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