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Band structure of [100] surface of $Cd_{1-x}Mn_xTe$ diluted magnetic semiconductor

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Electronic band structure of the diluted magnetic semiconductor $Cd_{1-x}Mn_xTe$ [100] ideal surface is calculated by the semiempirical tight-binding method in the framework of sps*-model. Surface bands, emerging above the bulk band structure, as well as their type, energy position and localization near the parting border with vacuum are investigated. It is shown that Mn $3d$-states as well as sp-states play appreciable role in the formation of surface bands. The peculiarities of surface band structure are analyzed in the dependence of solid solution composition.

Key words: *diluted magnetic semiconductor, band structure, surface*

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Semiconductor compound $Cd_{1-x}Mn_xTe$ represents a solid solution based on two semiconductors with zinc-blende structure: CdTe and MnTe, in which the part of nonmagnetic cations is replaced by an element of transition group Mn. The electronic band structure of semiconductor compounds with magnetic components is thoroughly studied, both theoretically and experimentally [1–4]. sp-type bands of such semiconductors show the behaviour similar to sp-bands of the nonmagnetic material, and magnetic $3d$-states of Mn form bands which split up due to strong coulomb and exchange interactions. The majority of optical and magnetic properties of diluted magnetic semiconductor (DMS) $Cd_{1-x}Mn_xTe$ can be explained by the exchange interaction of sp-band and $3d$-states, as well as by Mn-Mn exchange interaction, which, in its turn, largely depends on the magnitude of sp-d hybridization [2].

The majority of recent works on DMS is devoted to the investigation of heterostructures (interfaces, superlattices, quantum holes), where one of the components is DMS $Cd_{1-x}Mn_xTe$ [5]. Due to this, the study of the electron band structure of DMS in the presence of a parting border and particularly the analysis of $3d$-states contribution to the band structure are very important. In the majority of theoretical approaches a pure atom (ideal) surface is used as a model system for the study of the semiconductor surface electron band structure. In the paper [6] we studied the energy structure of an [100] ideal surface of semicondutor CdTe, doped by an isolated transition group impurity. It is shown that in the case when the impurity substitutes an atom near the surface, essential reconstruction of its energy spectrum takes place. In the present work the electron band structure of an [100] ideal surface of DMS $Cd_{1-x}Mn_xTe$ and the contribution of Mn $3d$-states to the formation of surface states are being investigated.

The theoretical approach is based on a semiempirical tight-binding method the basis of which includes s-, p-orbitals of each atom, cations d-orbitals, and it takes into account the interaction with the nearest neighbours only [3]. Such a model gives an opportunity to obtain a realistic band structure over all Brillouin zone of the crystal that is difficult to achieve in the framework of more complicated first principles calculations [4] or using the $\vec{k}\vec{p}$-theory [2].

Let's consider in more detail the electron band structure of a bulk diluted magnetic semiconductor. The Hamiltonian of the crystal in the tight-binding method has the following form:

$$H = H_{sp} + H_d + H_{sp-d}\,. \tag{1}$$

Here H_{sp} is a usual band Hamiltonian of A^2B^6 group semiconductor where cation d-orbitals and cation and anion s^*-orbitals are added to sp^3-basis. The latter take into account the presence of the excited conduction bands, and make it possible to describe more correctly the behaviour of the first conduction band [7]. The term H_d describes intracenter exchange-correlation effects in the half filled $3d$-zone, which we shall treat in the generalized Mott-Hubbard form [8]:

$$H_d = \sum_{i\mu\sigma}\left(\varepsilon_\mu n_{i\mu\sigma} + \frac{U}{2} n_{i\mu\sigma} n_{i\mu-\sigma} - \frac{J}{2}\sum_{\nu\neq\mu} n_{i\mu\sigma} n_{i\nu\sigma}\right). \tag{2}$$

Here $n_{i\mu\sigma}$ is an occupation number of $3d$-orbitals of type $\mu(\mu = t_{2g}, e_g)$ with spin σ on i Mn site. The parameters U and J are responsible for the intracentral Coulomb as well as exchange interactions, correspondingly. Despite of a manybody nature of the Hamiltonian (2), the band structure of DMS is well described in the one-electron approximation. Within the framework of this approximation, half filled Mn $3d$-band is splitted into two subbands, one of which is completely filled and lies in the valence band. The magnitude of splitting is $U_{\text{eff}} = U + 4J$ [3]. Thus, the ground state of the system is provided with all five $3d$-electrons pointed in one direction and the full magnetic moment on each site is equal to 5/2. The last term in (1) takes into account the interaction between $3d$-electrons and sp-bands.

The electron spectrum of $Cd_{1-x}Mn_xTe$ is calculated within virtual crystal approximation [1]. Matrix elements H_{sp} for two limiting CdTe and MnTe cases are expressed through tight-binding parameters [7,9], which were determined by the adjustment of spectrum in Γ and X points of the Brillouin zone to the known experimental and theoretical data. If for CdTe such a procedure can be accomplished directly through the use of experimental data, for hypothetical MnTe with zincblende structure in order to determine the tight-binding parameters we use first principles calculations of MnTe ferromagnetic phase [4]. It is necessary to distinguish two cases of spin direction on Mn sites: *up* (↑) and *down* (↓). The paramagnetic phase is received under the assumption that up and down spins are distributed in cation sites of the lattice at random. For parameterizations of the paramagnetic MnTe Hamiltonian it is necessary to average the tight-binding parameters for two possible spin directions. Therefore, in the virtual crystal approximation the spectrum of paramagnetic $Cd_{1-x}Mn_xTe$ is simulated by pseudo-ternary solid solution $Cd_{1-x}Mn\uparrow_{x/2}Mn\downarrow_{x/2}Te$ [3].

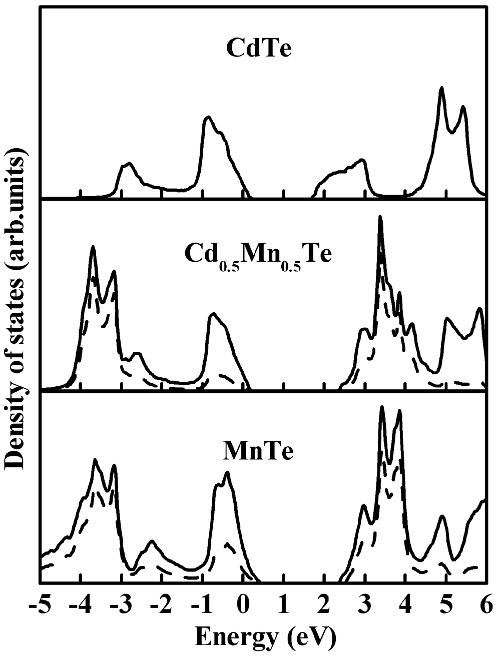


Figure 1. Electron states density of CdTe, MnTe and $Cd_{0.5}Mn_{0.5}Te$ semiconductors. Dashed lines correspond to the partial contribution of Mn $3d$-states.

The magnitude of the intracenter effective splitting U_{eff}, which determines the position of the occupied and unoccupied Mn-states, is crucial for the parameterizations of the Hamiltonian (2). By the research of synchrotron radiation and photoemission spectroscopy in $Cd_{1-x}Mn_xTe$ it is firmly established that the band of the occupied $3d$-states lies at the energy 3.4 eV, below the edge of the valence band E_v of the semiconductor [2,3]. The magnitude of $E_v - E_d$ = 3.4 eV practically does not depend on the concentration x. The placement of the unoccupied $3d$-states has evoked the greatest differences among researchers. However,the recent study of ultraviolet inverse photoemission from the conductivity band in $Cd_{1-x}Mn_xTe$ has made it possible to evaluate the magnitude of effective splitting in the limits $U_{\text{eff}} = 7.0 \pm 0.2$ eV [9]. Due to this, we can state that the bands of the unoccupied $3d$-states lie in the first conduction band approximately at the energy 3.6 eV. Another important parameter of the problem is V_{pd}, which defines the magnitude of *sp*-*d* hybridization. From general point of view, hybridization parameter must be different for two different spin configurations. The value for the parameter of *sp*-*d*-hybridization is taken directly from the experimentally measured *sp*-*d* exchange interaction constant. The evaluation gives for V_{pd} the following value V_{pd}= 0.219 eV [9]. As far as in the literature there is a unique value for the *sp*-*d* hybridization parameter, we consider a model in which these parameters are identical. As for the values of other tight-binding parameters for CdTe and paramagnetic MnTe as well as their corresponding discussion one can find in [11].

In figure 1 we present the densities of electron states for CdTe, paramagnetic MnTe and $Cd_{1-x}Mn_xTe$ with x=0.5, calculated by means of determined tight-binding parameters. The partial contribution of Mn $3d$-states is shown with a dashed line. As follows from the figure, there are two peaks lower than the valence band edge in the energy region 3–4 eV which correspond to the band of the occupied $3d$-states, split due to the sp-d hybridization. The bands of unoccupied states give a maximum somewhat above the bottom of the conduction band. Let's mark a significant contribution of $3d$-states to the valence band states in the region 0–2.5 eV. Our calculations of the electronic band structure of DMS $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ coincide, in general, with theoretical calculations of other authors.

A crystal, limited by an ideal surface, can be represented as a set of crystallographic planes, parallel to the plane, which forms the boundary of the crystal with vacuum. For the crystal with zinc-blende structure with an ideal surface perpendicular to the direction [100] each atomic plane contains the atoms of one type (cations or anions). The coordinate system is selected in a way that the axe OZ is directed parallel to the direction [100], and the axes OX, OY are directed along the basis vectors of the elementary translations of the two-dimensional lattice. The equilibrium position of any atom of such a structure is determined by the vector

$$\vec{R}(N_p lk) = l_1\vec{a_1} + l_2\vec{a_2} + \vec{\tau}_{\perp}^{p} + \vec{\tau}_{\parallel}^{pk}, \tag{3}$$

where N_p – the number of the atomic plane ($1\leqslant N_p < \infty$); l_1, l_2 – integers; $\vec{a_1}$, $\vec{a_2}$ – vectors of the elementary translation of the two-dimensional lattice; the vector $\vec{\tau}_{\perp}^{p}$ – indicates the position of the atomic plane N_p, relative to the surface, and the vector $\vec{\tau}_{\parallel}^{pk}$ – indicates the placement of k-type atom in the atomic plane N_p inside the two-dimensional cell (k = 1,2).

The eigenfunctions of the crystal, limited by [100] surface are characterized by the vector $\vec{k_{\parallel}}$, which lies in the two-dimensional Brillouin zone in the plane, perpendicular to the direction [100]. In the framework of the tight-binding model the crystal wave function is represented as a linear combination of atomic orbitals $\phi_{\alpha}(\vec{R})$, centered on the sites (3)

$$\Psi_{\vec{k}_{\parallel}a}(\vec{r}) = \sum_{\alpha N_p} c_{\alpha N_p}(\vec{k}_{\parallel}a)\phi_{\alpha N_p}(\vec{r}). \tag{4}$$

Here α runs over cation s-, p-, d-, s*- orbitals and anion s-, p-, s*-orbitals. In the base (4) the Hamiltonian (1), taking into account (2), gives the secular matrix for determining the electron spectrum of the crystal with the surface

$$|H_{\alpha N_p,\alpha N_p'}(\vec{k}_{\parallel}a) - E\delta_{ij}| = 0. \tag{5}$$

The Hamiltonian matrix (5) has got, generally speaking, an infinite dimension. In numerical calculations the surface is simulated by a slab, i.e. the semi-infinite crystal, which is limited by the second plane, that is identical to the plane forming the boundary of the crystal with vacuum [12]. Thus, the system is simulated by a slab of a finite width, but infinite in the direction, parallel to the surface. Our calculations showed that it is enough to select a slab consisting of 15–20 atomic planes. For such a width of the slab, the wave functions of the opposite surfaces are not overlapped any more and the electron spectrum practically does not depend on the inclusion of additional planes.

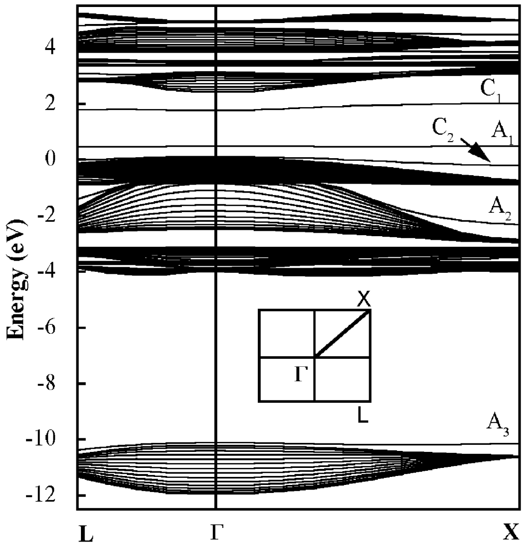


Figure 2. Electronic band structure of [100] ideal surface of DMS $Cd_{0.5}Mn_{0.5}Te$. In insertion, two-dimensional Brillouin zone is presented.

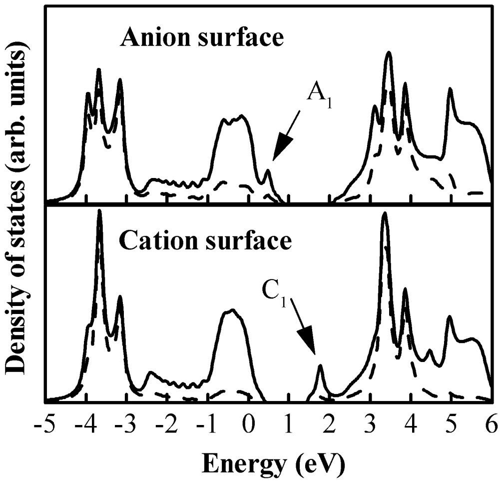
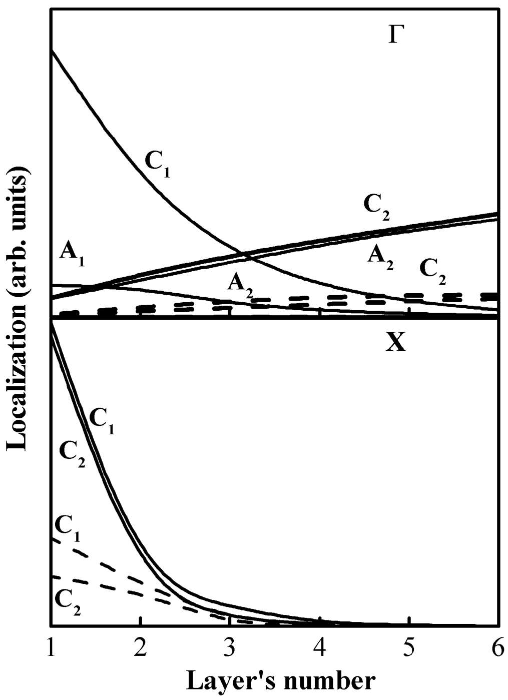


Figure 3. Electron states density of DMS $Cd_{0.5}Mn_{0.5}Te$ with [100] ideal surface, projected on the atomic plane which forms the parting border. Dashed lines correspond to the partial contribution of Mn 3*d*-states.

The band structure of an ideal [100] surface of DMS $Cd_{1-x}Mn_xTe$ (x=0.5), calculated along some high-symmetry directions of the two-dimensional Brillouin zone, is presented in figure 2. At the formation of the surface, surface bands appear in the spectrum of the bulk crystal due to breakdown of the bonds intrinsic to the crystal. As far as [100] the surface is polar, it is necessary to distinguish the two types of the surface, one of which contains cations on the parting border, and the other contains anions. The surface states for the two types of the ideal surface are presented in the same figure and designated correspondingly as C_i and A_i. We are interested in the bands which are situated in the forbidden band gap of the semiconductor or in the valence band and the first conduction band. For the anion surface, the three bands are being marked A_1, A_2, A_3, one of which – A_1 is located in the forbidden band gap of the semiconductor, somewhat above the edge of the valence band. The cation surface gives the two surface bands C_1 and C_2. In order to determine the contribution of Mn 3*d*-states to the formation of the surface bands of DMS $Cd_{1-x}Mn_xTe$ the projections of the full densities of electron states and partial contribution of Mn 3*d*-states on the surface which form the parting border of the crystal were calculated (figure 3). In the figure the peaks, which are absent in the density of states of the bulk crystal, correspond to the surface bands that specify space localization of the surface bands near the parting border. As follows from the figure, although the surface bands are mainly of *sp*-character they contain significant admixture of Mn 3*d*-states. The degree of localization of the electron density of the surface bands for a certain value of the wave vector depends on the position of the wave vector in the Brillouin zone of the crystal. In figures 4, 5 the dependence of the magnitude of localization for DMS



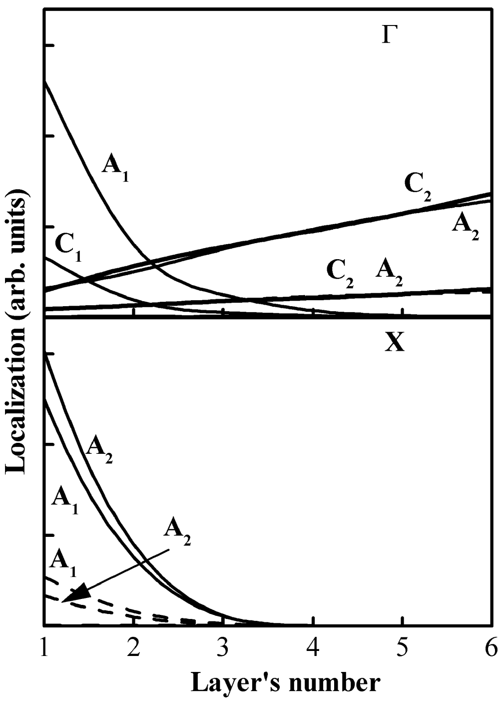


Figure 4. Degree of localization of surface states electron density near [100] $Cd_{0.5}Mn_{0.5}Te$ cation surface for two points in the Brillouin zone.

Figure 5. The same as in figure 4 but for the anion surface.

$Cd_{0.5}Mn_{0.5}Te$ on the distance to the surface is presented. As an example, the results for two high-symmetry points of the Brillouin zone – Γ and X are indicated. As follows from the figure, the electron densities of surface states A_i, C_i locate mainly on the planes which lie near the plane forming the parting border of the crystal with vacuum and practically disappear at the distance of 3–4 nuclear planes from the surface. The surface states in the band gap of the semiconductor – A_1, C_1 are localized in the Brillouin zone for all wave vectors, though in Γ point the localization is weaker. As for A_2-C_2-states which are in resonance with the valence band, a noticeable localization exhibits only for the wave vectors close to high-symmetry points of the Brillouin zone. In Γ point they are completely delocalized in the crystal. Qualitatively the same results for the localization of the surface states take place for $Cd_{1-x}Mn_xTe$ solid solutions with the other x.

The contribution of Mn 3d-states to the surface states depends mainly on the composition of $Cd_{1-x}Mn_xTe$ solid solution. The relative contribution of 3d-states to the surface states A_1, C_1 is presented in the table 1 for various x. The relative contribution of 3d-states increases with an increase of Mn component in the solution reaching the value of 20–30 % for x=0.75.

Energies of the surface states for $x < 0.5$ exhibit linear dependence on the composition of the solid solution (figure 6). If the dependence of the $Cd_{1-x}Mn_xTe$

Table 1. The relative contribution of $3d-$states to the surface states.

concentration	Γ		X	
	C_1	A_1	C_1	A_1
0.25	0.14	0.08	0.16	0.06
0.50	0.25	0.12	0.22	0.17
0.75	0.31	0.16	0.27	0.26

band gap in Γ point has a form E_g=1.62 + 1.61x, then for the energy dependence of A_1 states in Γ point, the linear coefficient is equal to 0.83, and for A_2 states it is equal to 0.55. Energies of the surface states in the Brillouin zone edges reveal a much weaker dependence on x.

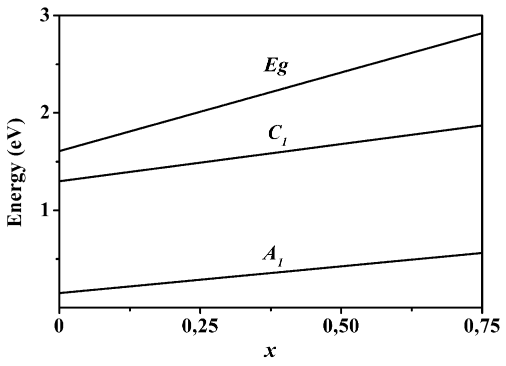


Figure 6. Dependence of energy of surface states A_1, C_1 in Γ point of the Brillouin zone on solid solution composition.

We can conclude that Mn $3d$-states give a noticeable contribution to the formation of the conduction and valence bands as well as to the formation of the bands of surface states. The carried out calculations let us analyze the magnitude of localization of electron densities of surface states and their energy in the dependence of the solid solution composition. Especially significant localization is observed for the surface states with the wave vector close to the Brillouin zone edges and with an increase of Mn content in the solid solution. The study of a model system (an ideal surface) can serve as a starting-point for the investigation of more complicated heterostructures, based on the diluted magnetic semiconductor $Cd_{1-x}Mn_xTe$.

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Зонна структура поверхні [100] напівмагнітного напівпровідника $\mathbf{Cd_{1-x}Mn_xTe}$

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Розраховано електронну зонну структуру ідеальної поверхні [100] напівмагнітного напівпровідника $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ в sps*-моделі сильного зв'язку, що включає катіонні d-орбіталі. Вивчено зони поверхневих станів, які виникають на фоні спектра об'ємного кристалу, їх тип, енергетичне положення та просторову локалізацію біля границь розділу з вакуумом. Показано, що поряд з sp-станами помітну роль у формуванні поверхневих станів відіграють $3d$-стани Mn. Аналізуються особливості спектра поверхні залежно від складу твердого розчину.

Ключові слова: *напівмагнітний напівпровідник, зонна структура, поверхня*

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