ELECTRONIC STRUCTURE OF ZINC-BLENDE Zn$_{0.5}$V$_{0.5}$Se: THEORETICAL STUDY*

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In this paper we present a comprehensive study of electronic structure of Zn$_{0.5}$V$_{0.5}$Se from the theoretical point of view. Partial and total density of states for spin-polarized antiferromagnetic phase of Zn$_{0.5}$V$_{0.5}$Se as well as schematic layouts of the bands have been obtained using the *ab initio* self-consistent semirelativistic linear muffin-tin orbital method.

PACS numbers: 71.20.−b, 71.20.Cf, 71.70.−d

1. Introduction

The band structure of ZnSe, obtained from an *ab initio* self-consistent semi-relativistic linear muffin-tin orbital (LMTO) method, has shown that this semiconducting compound is characterized by a direct energy gap ($\Gamma_8^v - \Gamma_6^c$). Moreover, on the basis of the results of calculations of partial density of states the valence band maximum has Se $4p$ character and the lowest band of the occupied valence states is mainly s-like and localized on an anion [1]. The introduction of a small amount of vanadium, which has non zero magnetic moment, transforms ZnSe into a II–VI diluted magnetic semiconductor (DMS). These materials have attracted considerable attention as a result of the large exchange interaction between the band electrons and d electrons of transition ions, the so-called sp–d exchange interaction [2]. Usually, the d states of a transition metal are split by this exchange interaction into two groups of sublevels with spin up and spin down.

2. Method of calculation

The partial and total densities of states for semimagnetic semiconductor $Zn_{0.5}V_{0.5}Se$ have been obtained using the *ab initio* self-consistent LMTO method [3, 4]. All relativistic corrections as well as a "combined correction term" [4] have been included in the calculations. The exchange-corrections to a local spin density approximation (LSDA) potential was used in the form proposed by Vosko–Wilk–Nusoir [5]. The calculations of the spin-polarized, antiferromagnetic phase were carried out in a hypothetical simple lattice for $Zn_{0.5}V_{0.5}Se$. We considered the zinc-blende structure of this material and applied the lattice constant equal 5.656 Å throughout the calculations. The openness of the crystal structure was dealt in a standard way by placing additional "empty spheres" into the unit cell [6]. The alloy environment in $Zn_{0.5}V_{0.5}Se$ has been simulated by an ordered supercell of $Zn_2V_2Se_4 + 8$ empty spheres. Two vanadium atoms with opposite spins were treated as two different types of atoms. All the calculations were carried out in a single energy panel, using $4s$, $4p$ and $3d$ basis functions for Zn; $4s$, $4p$ and $4d$ functions for Se, and $4s$, $4p$ and $3d$ for V. The self-consistency criterion was that the difference between the input and the output potential should be smaller than 0.001 Ry. The number of the $79k$ points were used in the irreducible Brillouin zone (1/12) during the numerical procedure.

3. Numerical results

The results of calculations for $Zn_{0.5}V_{0.5}Se$ are presented in Figs. 1 and 2. Figure 1a illustrates the chosen schematic layouts of the self-consistent bands for $Zn_{0.5}V_{0.5}Se$ deduced from the potential-parameter-related quantities B_l, C_l and A_l that specify the square-well pseudopotential: the bottom, the band center and the top of the l bands, respectively [4]. In Fig. 1b total density of states (states with spin up and down) resulting from our calculation is presented. The zero of the energy scales in Figs. 1a and b is at the Fermi energy. It is known that the LMTO method cannot reliably describe bands positioned higher than 1–2 Ry above the interstitial potential. Because of this, the energy ranges of figures are limited to 15 eV above the Fermi level. As it can be seen from Fig. 1, the theoretical alloy $Zn_{0.5}V_{0.5}Se$ shows metallic properties although ZnSe and hypothetical zinc-blende VSe compound belong to the wide gap semiconductors [7]. For a fixed l-band ($l = s$, p and d), a direct comparison between the layouts of ZnSe [1] and $Zn_{0.5}V_{0.5}Se$ does not show significant changes in energy positions of B_l, C_l and A_l for Zn and Se sites. However, one should notice the following tendency: the layout for all Zn l-bands in $Zn_{0.5}V_{0.5}Se$ spread out while all Se l-bands are narrowed in comparison with a pure ZnSe [1]. We have also obtained partial densities of states on each site and these results are given in Fig. 2, where zero of the scale is at the Fermi energy. Note that in Fig. 2 some curves (either d or s) are scaled in order to show them in the same scale. The lowest occupied states in the presented energy range are mainly s-like and localized on an anion. These states are shifted further from the Fermi energy by about 0.5 eV, as compared with a pure ZnSe [1]. The d states of Zn are located above the Se-s band as it was for pure ZnSe [1] and positions
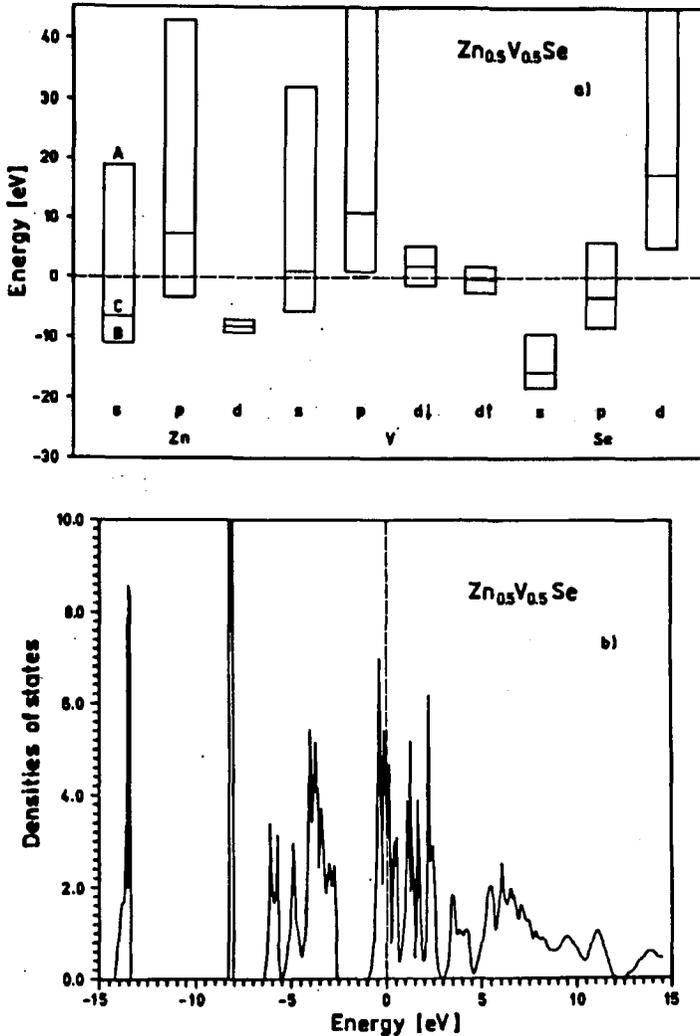
Fig. 1. (a) The schematic of the most important layout of the electronic structure of $Zn_{0.5}V_{0.5}Se$. The bars depict the extent of the n, l bands as defined by the parameters A_l (top of the band), C_l (band centre) and B_l (bottom of the band). (b) Total density of states for $Zn_{0.5}V_{0.5}Se$. The zero of scales is at the Fermi energy.

of these d states are changed downward in comparison with pure ZnSe by the order of 2 eV (counted from the Fermi energy). The Zn-$3d$ bands fall between the lowest Se-s like states and upper broad Se-s and Zn-p like bands, like in pure ZnSe, but Se-s and Zn-p derived bands are shifted towards lower energy by the order of 2 eV. Summing up, in the region from -15 to -2 eV, the electronic structure of $Zn_{0.5}V_{0.5}Se$ is very similar to pure ZnSe, but all states are shifted towards lower energies. The electronic structure for energy higher than 5 eV (measured from the
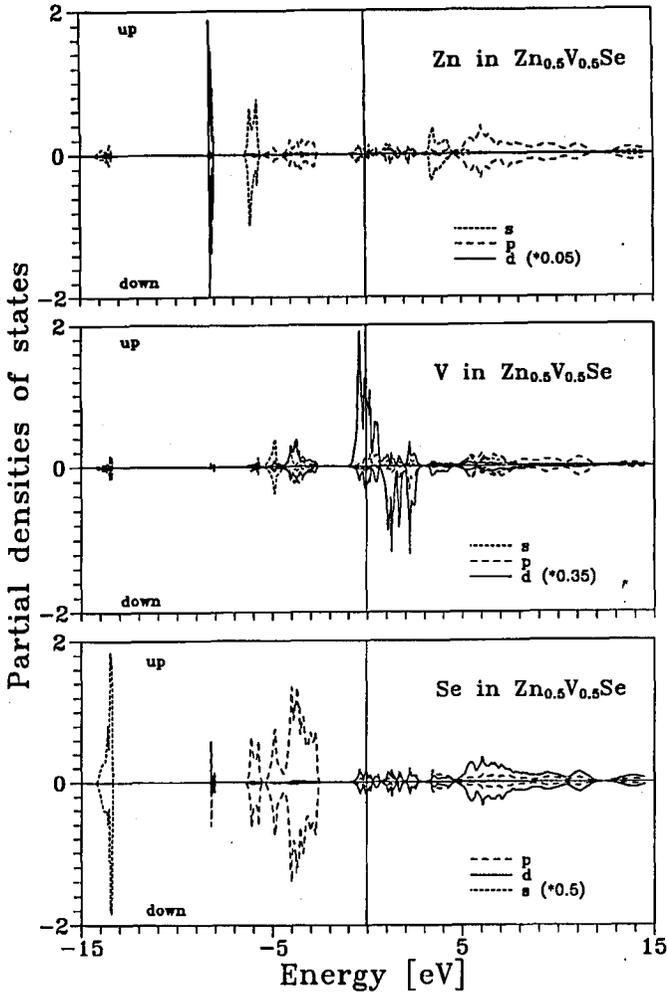
Fig. 2.   Partial density of states for sites Zn, V and Se in $Zn_{0.5}V_{0.5}Se$. The zero of scales is at the Fermi energy.

Fermi energy) follow by predominantly Zn-p states and Se-d states with appreciable contribution from V-p states. This behaviour is typical for all transition metals in ZnSe [7]. The d states of the transition metal and a cation in II–VI DMSs play a very important role in determining the electronic structure and electro-optical properties of these materials. From Fig. 2 for V in $Zn_{0.5}V_{0.5}Se$ the polarization of the V-d electrons is clearly seen. The main part of the V-d states is localized closely to the Fermi energy (zero in scale) and plays a main role in transformation of a ZnSe semiconductor into a metallic compound of $Zn_{0.5}V_{0.5}Se$. Moreover, the electronic structure of $Zn_{0.5}V_{0.5}Se$ is determined by these V-d electrons in the energy region 1–3 eV. The d states with spin up are centred at −0.2 eV and in

the main part occupied, whereas the spin-down d band is empty and centred at $+1.76$ eV (Figs. 1a and 2). The separation of $+1.92$ eV between them constitutes the effective d bands exchange splitting and seems to be a reasonable value as compared to other transition metals in ZnSe [7]. From Fig. 2 it is clear that the V-d electrons do not hybridize with the p states of an anion, which are separated from the main population of the d states of vanadium by about 2 eV. It is worth noting that valence bands of pure ZnSe are derived from the p states of an anion and the interaction of the V-d and p states of Zn gives some changes in position of Zn-p states with respect to the Fermi level. For $Zn_{0.5}V_{0.5}Se$ we do not find any negative splitting of anion p states due to p–d interaction exchange, like in ferromagnetic $Cd_{0.5}Mn_{0.5}Te$ [8]. In the $Zn_{0.5}V_{0.5}Se$ the energy positions of the main part of V-d and Se-p bands do not coincide. The electrons at the Fermi level do not fully polarize and the splitting of the top of the Se-p like band does not occur. Our calculations allowed us to obtain the magnetic moment for vanadium in $Zn_{0.5}V_{0.5}Se$ which is equal to $1.83\mu_B$. This value shows that the moment-reducing hybridization may be large.

4. Conclusions

Our calculation shows that the theoretical alloy $Zn_{0.5}V_{0.5}Se$: (1) demonstrates metallic properties, (2) does not have any negative splitting of p anion states due to the interaction p-d, moreover, p states from an anion do not hybridize with V-d states. Next, (3) an energy region from -15 to -2 eV is similar to pure ZnSe, but all states are shifted toward lower energy, (4) a region up to 5 eV is followed by predominantly Zn-p states and Se-d states with the appreciable contribution from V-p states, (5) d states of vanadium split into two sublevels (spin up and down) with the separation equal $+1.92$ eV, (6) V-d states with spin up are mostly occupied, whereas V-d states with spin down are unoccupied.

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