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Ab initio search of novel bipolar magnetic semiconductors: layered YZnAsO doped with Fe and Mn

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Very recently, the newest class of spintronic materials, where reversible spin polarization can be controlled by applying gate voltage: so-called bipolar magnetic semiconductors (BMSs, X. Li et al., arXiv:1208.1355) was proposed. In this Letter, a novel way to creation of BMSs by doping of non-magnetic semiconducting 1111 phases with magnetic $d^{n<10}$ atoms is discussed using ab initio calculations of layered YZnAsO doped with Fe and Mn. In addition, more complex materials with several spectral intervals with opposite 100% spin polarization where multiple gate-controlled spin-polarization can be expected, are proposed.

One of the main factors of the progress in spintronics [1], i.e. spin electronics, which makes use of the phenomena of spin-polarized transport in metals or semiconductors [2, 3], is the search of novel materials applicable for high-performance spintronic devices.

At present, much attention is focused on *magnetic half-metals* (MHMs). These materials, which were predicted in 1980s [4], are metallic for one spin direction, while semiconducting for the other spin direction, Fig. 1. For these systems, full spin polarization occurs at the Fermi level: $P = \{N^{\downarrow}(E_F) - N^{\uparrow}(E_F)\}/\{N^{\downarrow}(E_F) + N^{\uparrow}(E_F)\} = 1$, providing completely spin-polarized current.

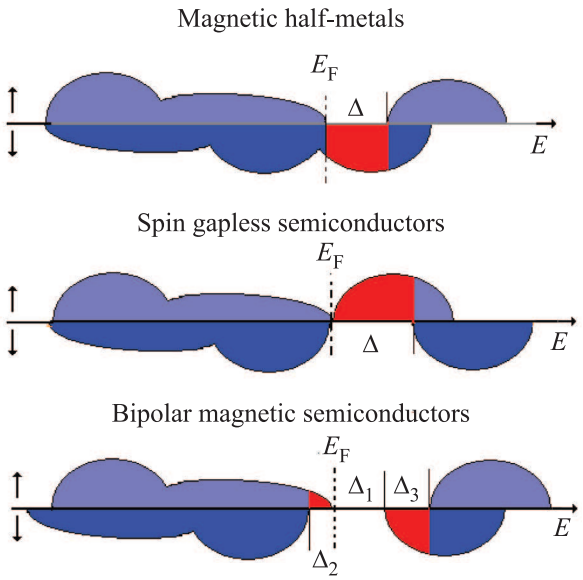

Fig. 1. (Color online) Schematic spin-resolved DOS pictures for spintronic materials: MHMs, SGSs and for the recently proposed [7] BMSs. The near-Fermi spectral regions of 100% spin polarization are shown in red. Δ_1–Δ_3 are gaps proposed to describe the BMSs [7]

Recently, one more interesting type of spintronic materials: so-called *spin gapless semiconductors* (SGSs), was proposed [5]. For these systems, one spin channel is gapless (like for known gapless semiconductors [6]), while the opposite spin channel is semiconducting, Fig. 1. For SGSs, also 100% spin polarization ($P = 1$) takes place, and no energy is required to excite electrons from the valence to the conduction band [5]. Generally, for both MHMs and SGSs (which contain *one spectral region* with $P = 1$, Fig. 1) manipulations or control of spin-polarized current may be successfully achieved by applying an external magnetic field to switch the spin polarization direction.

Another possibility for manipulations and controlling of spin-polarized current arises by using the electric field, which can be generated locally. In terms of the band theory, the position of the Fermi level, E_F, can be varied by applying gate voltage.

Very recently, the newest type of spintronic materials called as *bipolar magnetic semiconductors* (BMSs), which allow the electrical control of spin polarization, was proposed [7]. In the spectrum of BMSs, the both spin channels are semiconducting, but they are shifted from each other so that the top of the common valence band (VB) and the bottom of the conduction band (CB) are formed by the states of the opposite spin channels, as depicted in Fig. 1. It was proposed [7] to describe the BMSs by three gaps (Δ_1, Δ_2, and Δ_3, Fig. 1), where $\Delta^{\downarrow} = (\Delta_1 + \Delta_2)$ and $\Delta^{\uparrow} = (\Delta_1 + \Delta_3)$ are gaps for spin down and spin up channels, and $\Delta^{\downarrow\uparrow} = \Delta_1$ is the common gap between VB and CB edges. Let us note that unlike MHMs and SGSs, which contain *one spectral region* with $P = 1$, for BMSs *two spectral regions* (Δ_2 and

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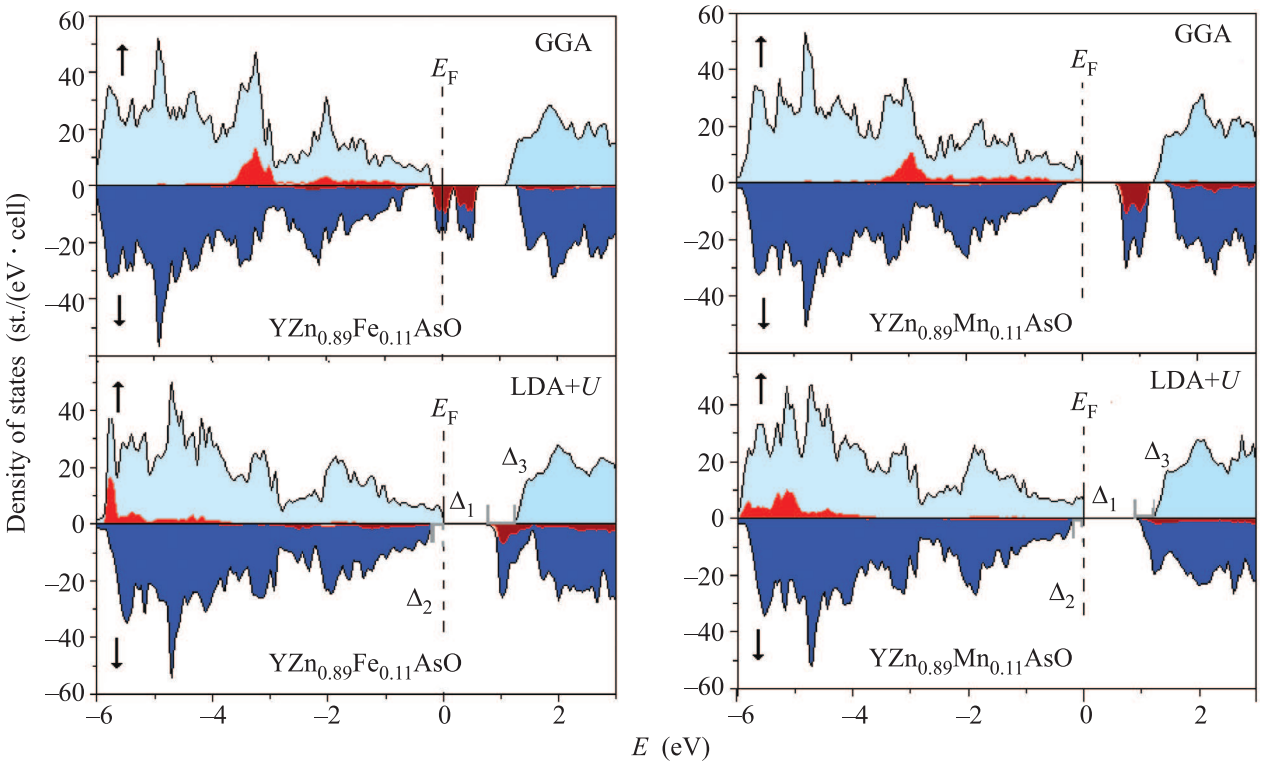

Fig. 2. Total and atomic (for Fe and Mn impurities) DOSs for $YZn_{0.89}Fe_{0.11}AsO$ and $YZn_{0.89}Mn_{0.11}AsO$ as obtained within GGA and LDA+U

Δ_3, Fig. 1) with $P = 1$ arise in each spin channel near the Fermi level.

It is assumed that alteration of the gate voltage sign and shifting of the Fermi level to the regions of Δ_2 or Δ_3 will lead to half-metallicity of BMSs with the different type of spin polarization. But as the first representative of the proposed BMSs the authors [7] discussed quite an exotic system: semi-hydrogenated single-walled carbon nanotubes. However, experimental preparation of such model systems (where hydrogen atoms should be adsorbed only on every second carbon atom of the tube wall) seems very problematic.

We believe that the family of BMSs can be essentially expanded, and in this Letter we propose the new 3D-like candidates of this interesting group of spintronic materials. We assume that one of the methods which may be used to design BMS materials is the tuning of the magnetic properties of the parent non-magnetic semiconductors by introduction of magnetic ions. Note that the doping strategy was very successful in search of other types of spintronic materials, such as MHMs or SGSs, see [8–13].

In our study we have chosen the tetragonal (space group $P4/nmm$, $Z = 2$) arsenide-oxide YZnAsO as a parent phase. This quaternary compound belongs to the broad family of so-called 1111 phases with ZrCuSiAs-like structural type [14, 15]. These 1111 phases became popular first of all as materials for so-called Fe-based superconductors, reviews [16–19]. Besides, the group of 1111 phases includes numerous semiconductors, which also have a large potential for applications owing to their outstanding physical properties, such as intense blue to near ultra-violet light emission, large third-order optical nonlinearity, etc. [20–23].

The arsenide-oxide YZnAsO has a quasi-two-dimensional crystal structure with alternating blocks [ZnAs] and [YO]. This phase is a non-magnetic direct-transition-type semiconductor with the gap at about 1.3 eV [24].

We have examined the effect of substitution of magnetic atoms M = Fe and Mn for the Zn atoms (inside the [ZnAs] blocks); and the nominal compositions $YZn_{0.89}M_{0.11}AsO$ have been simulated within the 72-atomic $3 \times 3 \times 1$ supercell, see details in [25]. The calculations were carried out by means of the full-potential method with mixed basis APW+lo (FLAPW) implemented in the WIEN2k suite of programs [26]. The plane-wave expansion was taken up to $R_{MT} \times K_{max}$ equal to 7, and the k sampling with $6 \times 6 \times 8$ k-points in the Brillouin zone was used.

Let us discuss the results obtained within the generalized gradient approximation (GGA) to exchange-correlation potential in the PBE form [27]. In Fig. 2, the total and partial (for Fe and Mn impurities) spin-resolved densities of states (DOSs) for $YZn_{0.89}Fe_{0.11}AsO$ and $YZn_{0.89}Mn_{0.11}AsO$ are depicted. We see that for $YZn_{0.89}Fe_{0.11}AsO$, the Fe $3d^{\uparrow\downarrow}$ spin splitting leads to partial filling of the Fe $3d^{\downarrow}$ states, which are placed in the gap of YZnAsO. As a result, $YZn_{0.89}Fe_{0.11}AsO$ adopts a nonzero density of carriers at the Fermi level for one spin projection ($N^{\downarrow}(E_F) > 0$), but has a gap for the reverse spin projection ($N^{\uparrow}(E_F) = 0$), i.e. this system should be characterized as a MHM.

On the contrary, for $YZn_{0.89}Mn_{0.11}AsO$, the Mn $3d^{\uparrow}$ states remain filled, whereas the Mn $3d^{\downarrow}$ states are shifted to the edge of the CB and become unoccupied. From Fig. 2 we can see that the obtained spectrum of this system resembles well the DOS picture for BMSs.

However, before declaring the Mn-doped YZnAsO as a bipolar magnetic semiconductor, we should confirm our result taking into consideration the possible role of correlation effects. To probe this issue, we have applied the local density approach with the on-site Coulomb interactions (so-called LDA+U technique [28]) using the well established [29] on-site Coulomb repulsion parameters $U = 6.8$ and 6.9 eV and Hund's parameters $J = 0.89$ and 0.86 eV for Fe and Mn, respectively.

The results reveal that the main effect of electronic correlations of $YZn_{0.89}Mn_{0.11}AsO$ is the growth of splitting of the Mn $3d^{\uparrow}/3d^{\downarrow}$ states, while this system retains the BMS-like spectrum, which is characterized by three gaps: Δ_1, Δ_2, and Δ_3, Fig. 2. In more detail (see Fig. 3), the near-Fermi regions with 100% spin polarization are formed mainly: for the majority-spin channel – by As states and mixed (Y+O) states, for the minority-spin channel – by contributions of mixed (Zn+As+Mn) and (Y+O) states for the blocks [ZnAs] and [YO], respectively. Our results show also that the electron-electron correlations lead to some changes in the gaps ($\Delta_1 = 0.52/0.82$ eV, $\Delta_2 = 0.76/0.98$ eV, and $\Delta_3 = 0.65/0.30$ eV, as calculated within GGA/LDA+U, respectively), as well as in the magnetic moments, which adopt $3.57\mu_B$ per Mn atom (within GGA) *versus* $4.17\mu_B$ as obtained within LDA+U.

Quite a different situation was observed for $YZn_{0.89}Fe_{0.11}AsO$. Here, the electronic correlations result in the total change of the spectrum type, which is transformed from MHM to BMS, when the Fe $3d^{\downarrow}$ states are shifted to the CB edge and become unoccupied forming $\Delta^{\downarrow\uparrow}$ gap between the VB and the CB, Fig. 2.

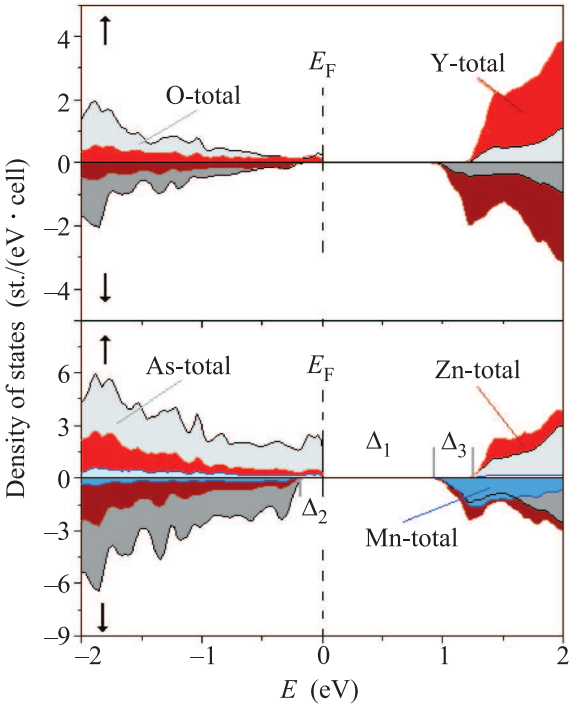

Fig. 3. Atomic-resolved spin densities for constituent blocks [YO] (upper panel) and [ZnAs:Mn] (bottom panel) of $YZn_{0.89}Mn_{0.11}AsO$ as obtained within LDA+U

In summary, our *ab initio* probing reveals that the non-magnetic semiconducting 1111 phases may be suitable matrixes for creating a new group of bipolar magnetic semiconductors by their doping with magnetic $d^{n<10}$ atoms. In turn, the broad family of prepared 1111-like layered semiconductors (reviews [14, 15, 21–23]) with variable gaps and good chemical flexibility to various atomic replacements forms a huge "reservoir" for future search of BMSs with the variable gaps $\Delta_{1,2,3}$. Let us also note that such theoretical search of new BMSs by doping should include the correlation effects.

Finally, we assume that, besides BMSs, at least some other more complex materials with "combined"-type spectra may be expected, for example MHMs/BMSs or SGSs/BMSs, which can provide a new platform and new opportunities for spintronics, electronics, and optics. The obvious way to construct such materials is to create in the gap of BMS a spin-polarized band of a magnetic impurity, as shown in Fig. 4. In this case, already four spectral intervals with 100% spin polarization arise, while for one material, as depending on the Fermi level position (I–V), the situations of MHM (I, III, IV), SGS (II) or BMS (V) can take place. By applying gate voltage for required shift of the E_F, the multiple variants of controlled spin-polarization can be provided.

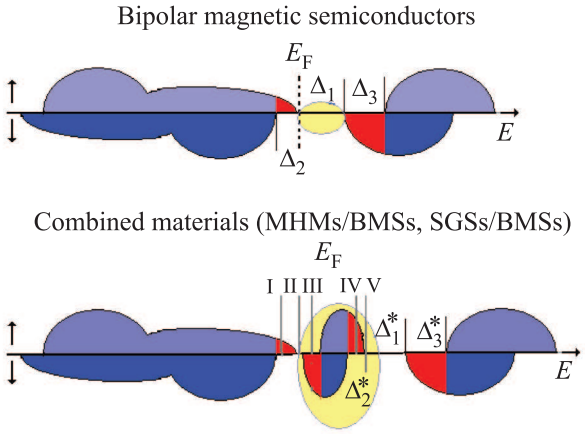

Fig. 4. (Color online) Schematic picture of formation (by doping of BMS with a magnetic impurity) of the proposed materials with several spectral intervals with opposite 100% spin polarization (shown in red), where multiple gate-controlled spin-polarization can be expected. I–V are possible positions of the Fermi level (see the text)

We believe that the aforementioned high chemical flexibility of the considered 1111-like layered semiconductors enables the co-doping procedures, which seem to be a possible way to create the discussed materials. Certainly, further theoretical and experimental efforts are necessary in the development of the proposed systems, which can promote the expansion of the palette of modern spintronic materials.

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