

Influence of spin polarization of p electrons of anions on a spin state of transition metal ion doped in ZnVI semiconductors. GGA+U calculations

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II-VI and III-V semiconductors (DMS) doped with transition metals (TM) were the focus of last decade research. A special attention was paid to wide band semiconductors, like ZnO:Mn, due to the predicted ferromagnetism (FM) at room temperature [1, 2]. However semiconductors with p-type conductivity are difficult to fabricate because of the undergoing compensation.

A number of works [3, 4] suggested that p orbitals of anions like, N, O or S may play a crucial role in magnetism of DMS. It is obvious if we consider *sp-d* hybridization lying at the base of magnetic properties in DMS [3]. Moreover, magnetic properties stem from properties of valence bands that are built mainly from p orbitals of anions. Here, the influence of anions comprising the material matrix is investigated and analyzed within the ab-initio studies. We analyze an electronic structure and magnetic properties of zinc-blende ZnO, ZnS, ZnSe, and ZnTe doped with TM ions as Mn, Fe, Co or Re by Density Functional Theory calculations within the generalized gradient approximation (GGA). We included the Hubbard-like term +*U* describing the on-site Coulomb interactions [5]. Calculations were performed using QUANTUM-ESPRESSO code [6]. We assumed that *U* range from 0 to 10 eV, and applied the correction to *d*(Zn), *d*(TM), and 2*p*(O) states. The *zb*-supercell used in calculations contained 64 and 216 atoms.

Electronic structure of TM substituting cation in II-VI crystals is determined by its local atomic configuration and TM-induced bands can be regarded as combinations of the *d*(TM)-*p*(anion) states. In *zb*-crystal field a doublet and a triplet (which is higher in energy by ~1 eV) *d*(TM) bands are split into spin-up and spin-down states by the exchange coupling ($\Delta\epsilon_{ex}$). Stability of high spin state (HS) of defect is determined by an energy of spin polarization (ΔE_{sp}), corresponding to a difference in total energies of spin nonpolarized (PM) and polarized (FM) states.

Calculations of density electronic states and density of spin polarizations for considered system show that spin polarization of defects originates from a spin polarization of *d* orbitals of TM and *p* orbitals of anions, mainly those that are neighbors of the TM ion. Moreover, it is shown that both, ΔE_{sp} and $\Delta\epsilon_{ex}$ depend on energies of spin polarization of both *d*(TM) and *p*(anion) orbitals. We analyzed a dependence of stability of HS state of TM on charge state of TM. Results of GGA+U calculations for neutral TM are shown in Table I.

Table I Energy of spin polarization (eV) and a total spin of TM ions in ZnVI semiconductors

	ZnO	ZnS	ZnSe	ZnTe
Mn _{Zn}	5.93 (S=5/2)	5.5 (S=5/2)	5.4 (S=5/2)	5.6 (S= -5/2)
Fe _{Zn}	4.64 (S=4/2)	3.3 (S=4/2)	2.83 (S=4/2)	3.3 (S= -3.2/2)
Co _{Zn}	3.4 (S=3/2)	2.8 (S=3/2)	2.54 (S=3/2)	2.0 (S=-2.9/2)
Re _{Zn}	4.0 (4.6/2)	3.8 (S=5/2)	0.63 (S=1/2)	4.0 (4.5/2)

The biggest spin polarization energy is reported for ZnO and ZnS and can be associated with strong spin polarization of p orbitals of O (S) atoms near the defects.

Spin density calculations suggest that for defects spin density is localized in the vicinity of both the TM and the nearest-neighbor four anion atoms. A degree of delocalization of a wave function of TM in ZnVI increases with a increasing atomic number of TM and with a decreasing atomic number of anions. In case of Co and Re, spin density function exhibits a long-range and more delocalized character in ZnO and ZnS.

Calculations of spin density indicate a frustrated magnetism for Re ion in ZnO and ZnSe, since *d*(Re) and *p*(O) (*p*(Se)) of oxygen neighbors have opposite spin polarizations. In ZnSe, Re_{Zn} is a low spin state with a spin equal to ½. Finally, the impact of the assumed value of *U*(TM) on the magnetic properties of ZnVI:TM is analyzed.

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