Electronic and magnetic properties of isolated Re(vs Mn) ion and Re-Re (vs Mn-Mn) complex in wurtzite - and zinc blende – ZnO in GGA +U approach

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In the field of spintronics, dilute magnetic semiconductors that combine nonvolatile magnetic storage and traditional electronics can offer the possibility of spin polarized current and electrical control of magnetic effect. Ferromagnetism (FM) in p-type Mn-doped ZnO, predicted by T. Dietl in 2000 [1], is one of the most widely studied and controversial transition metal (TM) doped oxide semiconductor systems. Significant array of contradictory results were obtained for this system stating FM [2], AFM, PM, and spin glass phase in ZnMnO [3]. The mechanism of FM in transition metal (TM)-doped oxide semiconductors remains unclear, because the observed magnetism can be either an intrinsic property of the material, or a result of the formation of secondary magnetic phases due to precipitation of TM clusters. At present, two explanations of magnetism in TM-doped ZnO are operative. One approach is based on the Zener model [3], and the second one relies on the first principles calculations showing that the overlap of d(TM) with p orbitals of neighboring O atoms form delocalized band levels, and an exchange interaction depends on density of (spin polarizized) states at the Fermi level [4]. It was shown that wave function of Mn ion in ZnO is strongly localized on Mn states and magnetic interaction between Mn-Mn is short range [3]. Delocalization of impurity-induced bands may be responsible for long-range magnetic interactions.

To check this hypothesis we analyzed properties of isolated rhenium Re^{2+} ion in wurtzite (w) and zince blende (zb) crystals and magnetic interaction Re-Re by Density Functional Theory calculations within the generalized gradient approximation, and compared them with the respective results for Mn. 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 $0<U<10$ eV, and applied the correction to d(Zn), $d($Re(Mn)), and $2p$(O) states. Application of U(Zn) = U(O) = 7 eV gives a correct value of a band gap of ZnO, 3.2 eV. The w- (zb) - supercell used in calculations contained, 72, 128 (64, 216) atoms.

$5d$(Re) orbital, like $3d$(Mn), is occupied by 5 electrons. GGA+U calculations show that in w-ZnO the Re ion introduces a triplet and a doublet in the band gap and that the spin states of isolated ion are high spin (HS) with spins that equal to 5/2 and 2, for neutral (d^5) and 1+(d^4) charge states (q), respectively. In zb-ZnO, a stable HS configuration with spins 2 and 3/2 are identified for Re in q=0 and 1+, respectively. For small values of U, the low spin state is stable. In contrast to Re, Mn ion is in the high spin state within both GGA and GGA+U.

Calculations of spin density indicate a frustrated magnetism for Re ion, since d(Re) and p(O) of oxygen neighbors have opposite spin polarizations. Calculations of the density of the states of a pair Re-Re were performed. In contrast to the case of a Mn-Mn pair, spin polarization of a Re-Re pair is long-ranged due to the large radius of Re atom. In p-ZnO, the 2+ charge state of the Re-Re complex has the FM ground state, in contrast to a neutral pair in intrinsic ZnO, which exhibits a ferrimagnetic ground state. *Finally, the impact of the assumed value of U(Rh) on the magnetic properties of ZnO:Rh is analyzed*.

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