Electronic and magnetic properties of Cu in wurtzite bulk and quantum dot (QD) ZnO: GGA +U approach

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Transition metal atom doped ZnO is one of the most promising dilute magnetic semiconductors for various applications in optoelectronic and spintronics [1]. Theoretical [2-4] and experimental [4-7] studies suggested that Cu substituting for the divalent Zn in ZnO introduces the Cu^{2+} (d^9) level located in the band gap. A wide array of different results were obtained in support for collective magnetism in ZnO:Cu in both bulk and nano structures [4-8]. Electronic structure of an isolated ion and the origin of ferromagnetism of Cu doped ZnO are still controversial and open research questions, both in theory and experiments.

Calculations were performed using QUANTUM-ESPRESSO code [9]. We analyzed properties of isolated Cu^{2+} ion in wurtzite (*w*) bulk and QD ZnO and magnetic interaction of Cu-Cu by Density Functional Theory calculations within the generalized gradient approximation. We included the Hubbard-like term +U describing the on-site Coulomb interactions [10] applied on the *d*(Zn), *d*(Cu), and *p*(O) orbitals. Application of U(Zn) =10 and U(O) = 6 eV gives a correct value of a band gap of ZnO, 3.3 and 4.4 eV for bulk and ~1.5 nm quantum dot (QD) [11], respectively. The *w*- supercell used in bulk calculations contained 128 atoms. We constructed *w*-ZnO QD of nearly spherical shape with diameter ~1.5nm ($Zn_{84}O_{84}H_{114}$). Here, H is pseudo hydrogen atom with nuclear charge amounting to 0.5 or 1.5 depending whether it terminates the surface of O^{2-} or Zn^{2+}, respectively. Vacuum level was ~ 1.5-2nm.

Bulk ZnO. Results of calculations suggested that Cu^{2+} doublet (e_2) and triplet (t_{2g}) levels are in the band gap. e_2 and t_{2g} are split by exchange energy into spin up (e_2, t_{2g})$\Uparrow$ and spin down (e_2, t_{2g})$\Downarrow$ located about 0.2, 0.75, 0.8, and 1.4 eV above valence band maximum (VBM). The ground state of Cu in ZnO is in high spin state with spins 1/2 and 1, for neutral (d^9) and 1+ (d^8) charge states, respectively. Cu^{1+} (d^{10}) which is in the low spin state, introduces defect levels close to conduction band minimum.

QD ZnO. The Cu^{2+} ion sits in the core of the QD at the largest possible distance from the surfaces. The ground state in Cu^{2+} is in high spin state with total spin ½. Calculation of the density of states and spin density of Cu in QD ZnO show that the defect states and magnetic moments come from *d*(Cu) with a large contribution of *p*(O) orbitals of the O nearest neighbors of Cu.

Finally, the impact of the assumed value of U(Cu) on the magnetic properties of ZnO:Cu is analyzed. For U(Cu) >2 eV, the low spin state is stable.

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