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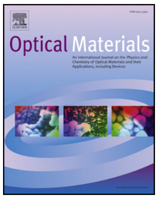

Transition metal ions in ZnO: Effects of intrashell coulomb repulsion on electronic properties

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ABSTRACT

Electronic structure of the transition metal (TM) dopants in ZnO is calculated by first principles approach. Analysis of the results is focused on the properties determined by the intrashell Coulomb coupling. The role of both direct and exchange interaction channel is analyzed. The coupling is manifested in the strong charge state dependence of the TM gap levels, which leads to the metastability of photoexcited Mn, and determines the accessible equilibrium charge states of TM ions. The varying magnitude of the exchange coupling is reflected in the dependence of the spin splitting energy on the chemical identity across the 3d series, as well as the charge state dependence of spin-up spin-down exchange splitting.

1. Introduction

Current interest in ZnO doped with various dopants stems from the recognized potential of ZnO in various applications. In particular, the usage of transition metal (TM) impurities was considered in various contexts, including both tunable magnetic properties and improved optical/transport properties [1–5]. A representative example is application of ZnO doped with Mn for photocatalysis [6]. A trivial statement is that controlled applications require a good understanding of electronic properties of the given dopant.

The present study is devoted to selected theoretical aspects of the physics of TMs dopants in ZnO. Our attention is focused on the role of the intrashell Coulomb coupling. To highlight characteristic features, we show the results obtained for the TM series from Ti to Cu, and discuss the trends displayed by their electronic structure, i.e., by energy levels, spin states, and accessible charge states. In a many body system, electron-electron coupling is realized through the direct as well as the exchange channel, the latter being a result of the antisymmetrization of the wave functions, and leading to the Hund's rule. Both channels determine the electronic structure of TM ions in ZnO.

Majority of TM ions induce states in the band gap of the host ZnO crystal. The ”deep” character of those states is reflected in the structure of the wave functions, which are mainly built up from the localized atomic-like *d* orbitals of the defect, while the contribution of the orbitals of its neighbors is smaller. Spacial localization in turn implies that the Coulomb repulsion between electrons occupying impurity levels is pronounced, and affects level energies by about 1 eV. (This is in contrast to the shallow and extended states, where the Coulomb energies are of the order of 0.01 eV) In most cases, a TM impurity can assume several charge states depending on the Fermi energy, which differ by the number of electrons that occupy impurity levels, and thus by the varying Coulomb intrashell coupling. In particular, with the increasing (decreasing) occupation of the defect gap level, its energy increases (decreases) as a result of the increased (decreased) Coulomb repulsion. This effect determines the possible charges states of the TM ion in ZnO.

A second consequence of the intrashell Coulomb coupling discussed below is the charge state dependence of the exchange coupling, revealed by the magnitude of the spin splitting of the TM levels. Finally, the third consequence of the strong localization of the wave function of the gap states is that the change of the charge state induces large variations of the distance between the TM ion and its nearest neighbors, which are of the order of a few percent. Such atomic relaxations affect the gap levels by about 1 eV.

Experimental investigations of TM in ZnO include optical and transport studies. Optical transitions observed in both absorption and emission can be either intracenter, i.e. between two levels of the TM ion, in which case the charge state of TM does not change, or the ionization transition, which excites an electron from the center to conduction band minimum (CBM), or from the valence band maximum (VBM) to the TM level. In the case of intracenter transition, the bond length between TM and its neighbors remain practically the same, and the transition energy is well approximated by the difference of the one electron eigenenergies of the gap states. On the other hand, ionization

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transitions imply pronounced atomic relaxations, and non-negligible Frank-Condon effect.

2. Method of calculations

The calculations are done by employing the generalized gradient approximation (GGA) to the density functional theory [7–9], supplemented by the + U corrections [10–12] meant to improve the agreement with experiment. We use the pseudopotential method implemented in the QUANTUM ESPRESSO code [13] with the valence atomic configuration $3d^{10}4s^2$ for Zn, $2s^2p^4$ for O and $3s^2p^64s^2p^03d^n$ or $4s^2p^03d^n$ for TM ions with n electrons on d (TM) shell. The plane-waves kinetic energy cutoffs of 30 Ry for wave functions and 180 Ry for charge density are employed. The electronic structure of the wurtzite ZnO is examined with a $8 \times 8\times 8$ $k-$point grid. Analysis of a single TM impurity substituting for the Zn lattice is performed using $3 \times 3 \times 2$ supercells with 72 atoms, while $k-$space summations are performed with a $3 \times 3\times 3$ $k-$point grid.

Theoretical description of the electronic structure of TM ions in semiconductors must begin with an accurate band structure of the host. In fact, underestimation of the band gap, typical for the local density approximation (LDA) or GGA will result in erroneous properties of dopants. For example, an underestimated band gap leads to a distorted electronic structure of TM when the TM state is predicted to be resonant with the continuum of the conduction band instead of being the gap state. As a consequence, wrong optical transition energies, metallic rather than insulating conductivity, and a non-correct type of magnetic coupling between TM atoms are obtained [14,15]. Here, a correct band gap is obtained by employing the + U corrections to the GGA calculations [16,17]. Application of + U correction only to d (Zn) [18,19] partially improves the situation. We find that applying the U correction also to p(O) orbitals, $U(\mathrm{O}) = 6.25$ eV, in addition to $U(\mathrm{Zn}) = 12.5$ eV, gives not only the experimental E_{gap} of 3.3 eV [20–22] but also the energy of the d (Zn) band, centered about 8 eV below the VBM [23]. Our U parameters for ZnO are similar to the values reported in other works [24–26]. Interestingly, the usage of hybrid functionals render a correct E_{gap}, but the agreement with experimental data for TM ions is far from satisfactory [27].

From our previous results it follows that the U corrections for the d (TM) orbitals are smaller than that used for d (Zn) in pure ZnO. While the inclusion of U (TM) improves the agreement with experiment, it turns out that the fitted U values are relatively small, and so are the energy changes. Typically, agreement with experiment is obtained for U (TM) of about $2-3$ eV [16,17,27]. A non-vanishing U (TM) implies occupation dependent corrections to the TM levels [16,17]. Since a comparison with the existing experimental data is beyond the scope of this work, we keep the discussion more transparent and highlight the impact of the Coulomb coupling by neglecting U (TM). The actual values of the U term for TM ions in ZnO were optimized by fitting the energies of ionization and intracenter optical transitions to experimental data [16,17].

Transition level between various charge states of a defect is defined as the Fermi energy at which formation energies of these states are equal. Our calculations are performed along the scheme proposed in Ref. [28] including the image charge corrections and potential alignment for charged defects [28–30].

The ionization energies are calculated as the total energy difference between the final and the initial states of the system. The thermal ionization energy can be obtained directly from the position of the $(+/0)$ level relative to CBM. The calculation of absorption-recombination transitions for Mn ion are performed with fixed occupation matrices at the Γ point [16]. In this case, the finite size corrections to the total energy are not necessary.

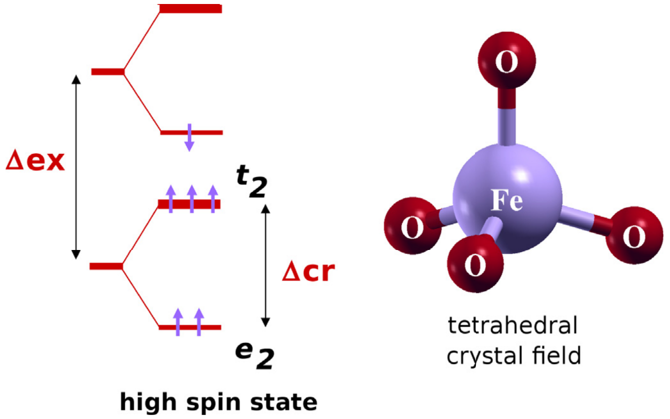

Fig. 1. Left panel: Schematics of the TM levels in ZnO, Fe^{2+} is taken as an example. Electron spins are shown by arrows, doublet (triplet) levels are denoted by thin (thick) lines. Right panel: the tetrahedrally arranged oxygen neighbors of Fe; in the wurtzite structure the three planar bonds are not equivalent with the vertical one.

3. Electronic structure od TM ions in ZnO

We begin by recalling that the electronic structure of a TM in a crystal follows from two effects. The first one is the exchange splitting of the d-electrons into spin up and spin down states following the Hund's rule. The second effect is the splitting of the d (TM) orbital quintet by the crystal field into a doublet and a triplet distant by about 1 eV. In the wurtzite ZnO, the latter is weakly split into a singlet and a doublet, typically by about 0.1 eV. This splitting is neglected in Figs. 1 and 2. The level structure is schematically shown in Fig. 1.

Both exchange and crystal field splittings are clearly visible in Fig. 2, which presents the calculated one electron energies of neutral TM^{2+} ranging from Ti to Cu. The relative magnitudes of splittings depend on the chemical identity of the ion, and are addressed below. In all cases, the exchange splitting exceeds the crystal field splitting, and all the TM ions are in the high spin state. Next, as it follows from the figure, with the increasing nuclear charge of TM, the levels decrease in energy [31]. Previous calculations [14] gave results similar to ours.

3.1. The dependence of the impurity levels on the charge state

The effect is exemplified in Fig. 3 for Ni. One can see that adding or subtracting one electron from $t_{2\downarrow}$ changes its energy by as much as ~1.5 eV. This demonstrates the magnitude of the intrashell Coulomb coupling, and makes the 1 + charge state of Ni unstable. Indeed, the capture of an electron on the $e_{2\downarrow}$ level increases its energy above the CBM, i.e., $e_{2\downarrow}$ becomes a resonance degenerate with the conduction band continuum. In such a case, autoionization of Ni^{1+} is expected to occur. On the other hand, removal of an electron from $e_{2\downarrow}$ of Ni^{2+}

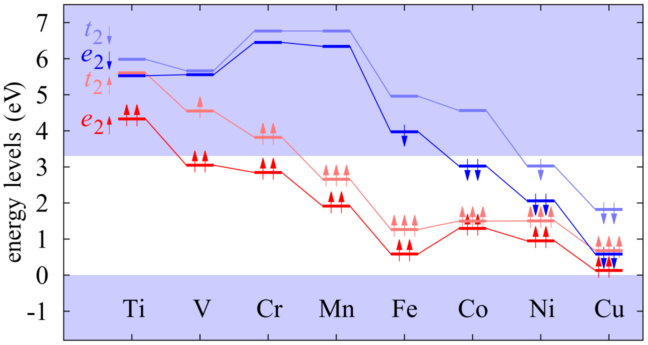

Fig. 2. Calculated d (TM) levels assuming U (TM) = 0. Small splitting of t_2 triplets is neglected. Arrows denote spins.