Ab initio study of magnetic properties of complexes formed by an Fe impurity and an intrinsic interstitial defect in ZnO

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By density factional supercell calculations we computed the total energy and the magnetic properties of isolated complexes formed in wurtzite ZnO doped with diluted Fe impurities in the presence of interstitial atoms of Zn or O. Interstitial O occupies preferentially a site with octahedral symmetry with substitutional Fe in the first neighbor shell, thus forming the complex Fe_{Zn}-I_O. In contrast, the complex Fe_{Zn}-I_{Zn} is energetically unfavored with respect to the case where the two components are far apart. For oxygen-rich growth conditions, a significant population of complexes Fe_{Zn}-I_O is stable at (and above) room temperature, providing a key to understanding the room-temperature magnetism of this system. Interstitial oxygen, coupled with diluted Fe impurities, exhibit a density of states spin polarized at the Fermi energy.

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I. INTRODUCTION

The possibility to build up artificial magnetic materials by doping with magnetic impurities at diluted concentration nonmagnetic semiconductors which are commonly used by microelectronic industry has driven increasing attention to the field of diluted magnetic semiconductors (DMSs). The main target is the design and realization of devices with novel functionalities determined by the electron spin rather that the electron charge as in conventional electronic devices. To be useful for the electronics industry, spin-electronic (or spintronic) devices must present an electron density at the Fermi level fully spin-polarized.[1] Further, a material to be employed in spintronic devices of commercial use must have magnetic properties stable at (and above) room temperature. In this contest, ZnO doped with transition metal impurities has attracted considerable interest due to the prediction of ferromagnetism at room temperature.[2] The room-temperature magnetic properties of this compound have been largely debated[3–5] due to several experimental works showing the presence[6–12] or the absence[13–15] of ferromagnetism at room temperature. Recently, the Mössbauer spectra of diluted ^{57}Fe have been interpreted on the basis of Fe^{3+} paramagnet centers on substitutional Zn sites with unusually long relaxation times.[16] According to recent room-temperature photoluminescence experimental results on ZnO irradiated with high-energy electrons, the major acceptorlike defects were determined to be oxygen interstitials and zinc vacancies.[17]

In our previous work[18] we have computed the formation energy and the magnetic properties of isolated complexes formed by Fe_{Zn} with intrinsic vacancies, finding that ZnO doped with diluted Fe impurities can exhibit a room-temperature concentration of complexes involving Zn vacancies that considerably influence the magnetic properties.

In the present paper, we complete the theoretical investigation presented in Refs. 18–20 by studying the formation energy of isolated complexes formed by interstitial oxygen I_O and by interstitial zinc I_{Zn} in Fe-doped ZnO.

II. COMPUTATIONAL DETAILS

Our simulations are obtained by plane-wave pseudopotential techniques with spin-dependent density functional theory and with generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE)[21] as implemented in the PWSCF package (plane-wave self-consistent field).[22] We use state-of-the-art ultrasoft[23,24] pseudopotential in the separable form introduced by Kleinmann and Bylander.[25] O pseudopotential has 6 valence electrons, while the Zn one has 12 valence electrons. We compute the formation energy by using a $3 \times 3 \times 2$ supercell (72 atoms for isolated Fe_{Zn} without vacancies) and relax atoms surrounding the defect within a radius of 3.95 Å in order to improve the convergence of the total energy with respect to the supercell size, according to the procedure adopted in Ref. 26 to study intrinsic defects in ZnO. The supercell lattice parameters are fixed to the bulk ones: $a = 3.28$ Å, $c = 5.30$ Å, obtained with the condition of vanishing stress and internal forces. The valence electronic density was expanded on a plane-wave basis set with a kinetic energy cutoff of 35 Ry, while for the augmentation density of ultrasoft pseudopotentials a cutoff of 560 Ry was used. Integration of electronic states is performed by means of special point techniques, by using (if not differently specified) a one-point Monkhorst-Pack[27] grid for the supercell and by means of smearing techniques in a similar way as done in Ref. 18.

For the charged defect, we computed the correction of repeated charges due to periodic boundary conditions according to the Leslie-Gillan method.[28] According to our calculation, the dielectric constant of the bulk system is almost isotropic: The component along c is $\epsilon = 4.89$ and the component along a is $\epsilon = 4.82$; that is, the difference between the two components is less than 2%. For this reason we take the average value ($\epsilon_{aver.} = 4.84$, considering the three Cartesian directions) when we compute the Leslie-Gillan correction.

III. THEORY

The defect concentration and the more stable configuration of complexes such as Fe_{Zn}-I_{Zn} (I_O) is determined by the

formation energy,[26] which for a (neutral) charged defect reads

$$\Delta E_f = E(N_{\mathrm{Zn}}, N_{\mathrm{O}}, N_{\mathrm{Fe}}) - N_{\mathrm{Zn}}\mu_{\mathrm{Zn}} - N_{\mathrm{O}}\mu_{\mathrm{O}} - N_{\mathrm{Fe}}\mu_{\mathrm{Fe}} + qE_F, \quad (1)$$

where $E(N_{\mathrm{Zn}}, N_{\mathrm{O}}, N_{\mathrm{Fe}})$ is the energy of the supercell containing N_{Zn} zinc, N_{O} oxygen, and N_{Fe} iron atoms; μ_α is the chemical potential of the α element (α = Zn, O, Fe); q is the charge of the defect (including its sign); and E_F is the Fermi energy. We conventionally take E_F to be zero at the top of the valence band and assume that its value can vary from the valence band edge up to the conduction band. Since, as usual in local density approximation, the fundamental band gap is underestimated ($E_g = 0.745$ eV according to our simulation), we take the experimental band gap of $E_g = 3.4$ eV for the energy range of E_F in a similar way as done in Ref. 29.

IV. RESULTS

A. Isolated intrinsic defects

Interstitial atoms in the wurtzite structure have two nonequivalent sites corresponding to two local minima of the energy: In one site the interstitial atom experiences a tetrahedral (tetra) symmetry; in the other site it experiences octahedral (octa) symmetry. For bulk ZnO, we found that the octahedral site is energetically favored with respect the tetrahedral one for both I_O and I_{Zn} defects. The O atom in the octahedral site has an energy that is -0.362 eV lower than the energy of O in the tetrahedral site, while for the Zn atom the octahedral site has an energy that is -1.999 eV lower than the energy of Zn in the tetrahedral site. According to our results, the Zn interstitial, I_{Zn} is not a magnetic defect; at variance, the interstitial oxygen, I_O, has a magnetic moment of $2.00\mu_B$ and $0.26\mu_B$ for the octahedral and tetragonal sites, respectively.

B. Neutral complexes

In Fig. 1 we display our results for the formation energy of the complexes Fe_{Zn}-I_O and Fe_{Zn}-I_{Zn}, as a function of Zn chemical potential. The lower values of μ_{Zn} corresponds to O-rich (or equivalently Zn-poor) growth conditions, the higher values to O-poor (Zn-rich) conditions.

We have considered the complexes in which the Fe_{Zn} is in the nearest-neighbor shell with respect the interstitial atom, giving two nonequivalent configurations for each interstitial site (octahedral or tetrahedra) considered. The formation energy of the configuration in which Fe_{Zn} and the interstitial atoms are infinitely far apart is also displayed (as a dashed line for O interstitial and as a dotted line for Zn interstitial). The zero of the energy corresponds to the formation energy of isolated Fe_{Zn}.

For the complexes involving I_{Zn} the configuration in which the Fe_{Zn} and the I_{Zn} in the octahedral position are infinitely far apart is energetically favored with respects to the configurations in which the Fe is in a neighbor shell with respect to I_{Zn}.

At variance, the complexes Fe_{Zn}-I_O have formation energy that is lower than the situation at which the Fe and the interstitial O are far apart. In particular, as shown in Fig. 1, the complex Fe_{Zn}-I_O with the interstitial oxygen in the octahedral position is energetically favored with respect to the complexes in which I_O is tetrahedically coordinated. Remarkably, for O-rich growth conditions (corresponding to the lower values of Zn chemical potential displayed in Fig. 1) the complex Fe_{Zn}-I_O (octa) has a formation energy that is comparable to the one of isolated Fe (the zero of the vertical scale in Fig. 1), allowing the formation of the complex Fe_{Zn}-I_O (octa) even at low temperature. For values of μ_{Zn} slightly higher than the minimum of μ_{Zn} in Fig. 1 the ΔE_f of Fe_{Zn}-I_O (octa) or of Fe_{Zn}-I_O (tetra) are still a fraction of an electron volt, allowing the formation of a significative population of this complex at room temperature. This situation is similar to the one found in Ref. 18, where the complex Fe_{Zn}-V_{Zn} with V_{Zn} in the next-nearest-neighbor shell with respect to Fe_{Zn} is found to have negative formation energy for Zn-poor growth condition.

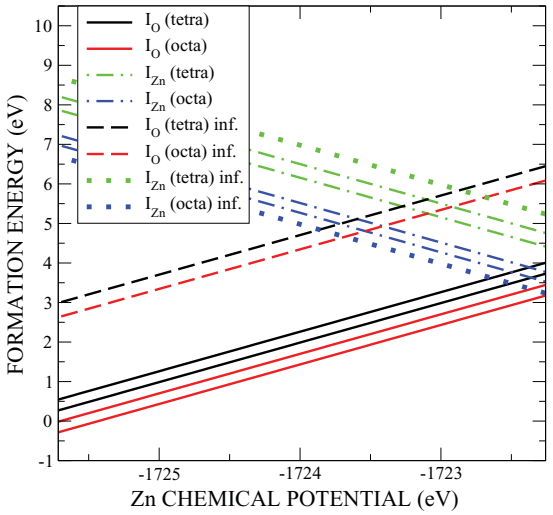

FIG. 1. (Color online) Formation energy of complexes Fe_{Zn}-I_O and Fe_{Zn}-I_{Zn} as a function of Zn chemical potential. The zero in the vertical axis corresponds to the formation energy of Fe_{Zn}.

To deal with a quantity that can be directly compared to experimental data, we have computed the binding energy of the complex, defined as the difference between the formation energy of the system when the intrinsic defect is infinitely far apart from the substitutional iron and the formation energy of the complex. For the two nonequivalent complexes Fe_{Zn}-I_O (octa) investigated we computed a binding energy 2.9 and 2.6 eV. For the two nonequivalent complexes Fe_{Zn}-I_O (tetra) investigated we computed a binding energy 2.7 and 2.4 eV; in the latter complex the I_O is placed, with respect to the Fe_{Zn}, along the direction determined by c lattice parameter of the wurtzite structure.

In Fig. 2 and Fig. 3 we display the relaxed structure of the complex Fe_{Zn}-I_O (octa) with lowest formation energy. The spin-density isosurfaces ($\pm 0.01\mu_B$) for majority and minority spin are also displayed in the same figures. From the figure one can notice the ferromagnetic coupling between the Fe and the interstitial O, while a small anti-ferro-magnetic coupling (minority spin) along the direction joining the Fe_{Zn} and the I_O. The total (absolute) magnetization per unit cell is 3.80 μ_B

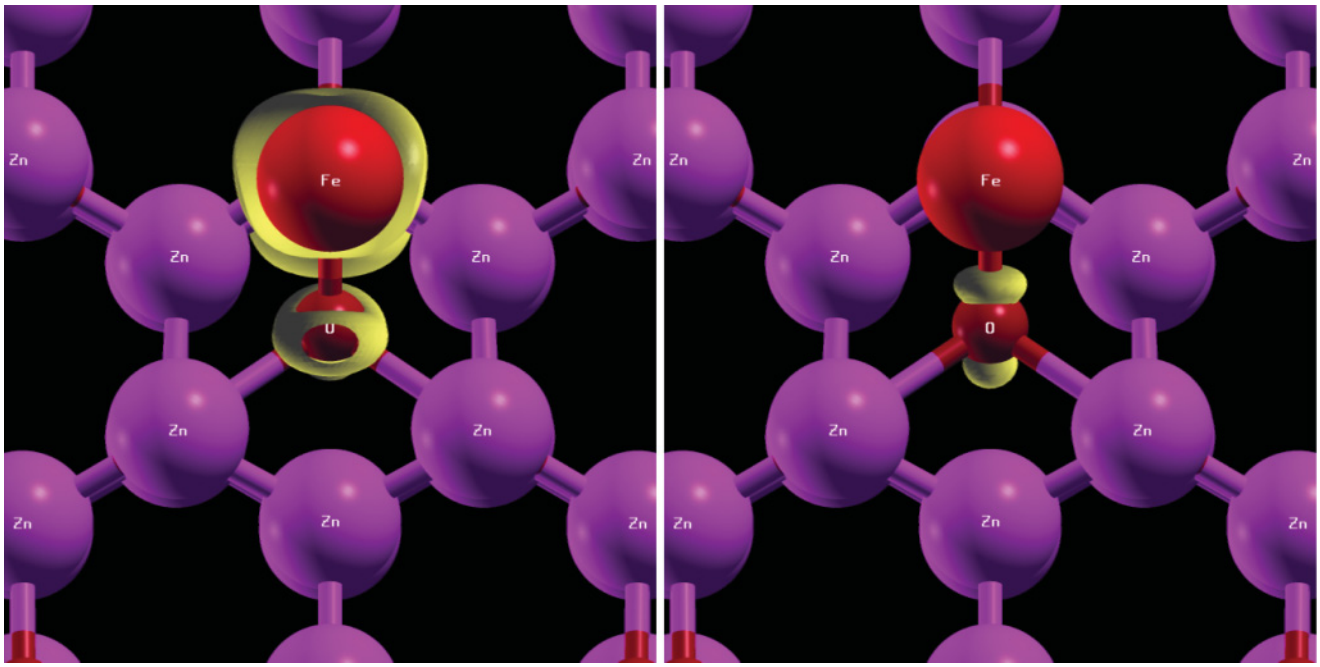

FIG. 2. (Color online) Top view of the complex Fe_{Zn}-I_O (octahedral site). In yellow are the isosurfaces for positive (0.01 a.u., left) and negative (−0.01 a.u., right) spin density.

(4.05 μ_B) while the total (absolute) magnetization of the other complex studied involving I_O at octahedral site is 4.03 μ_B (4.18 μ_B)

In Fig. 4 we display the spin-resolved density of state (SDOS) of the complex Fe_{Zn}-I_O (octa) that presents the lowest energy among those investigated. The Fermi energy is almost superimposed to the valence band maximum of the minority spin, while the band edge of the majority spin is approximately a fraction of an eV higher than E_F. The possibility that this complex can act as an acceptor is discussed in Sec. IV C.

In Fig. 5 we display the equilibrium configuration of the complex Fe_{Zn}-I_O (tetra) with lowest formation energy among the different configurations considered. The spin density isosurfaces ($\pm 0.01 \mu_B$) for majority and minority spin are also displayed in the same figures. The total (absolute) magnetization per unit cell is $3.88 \mu_B$ ($4.05 \mu_B$), while the

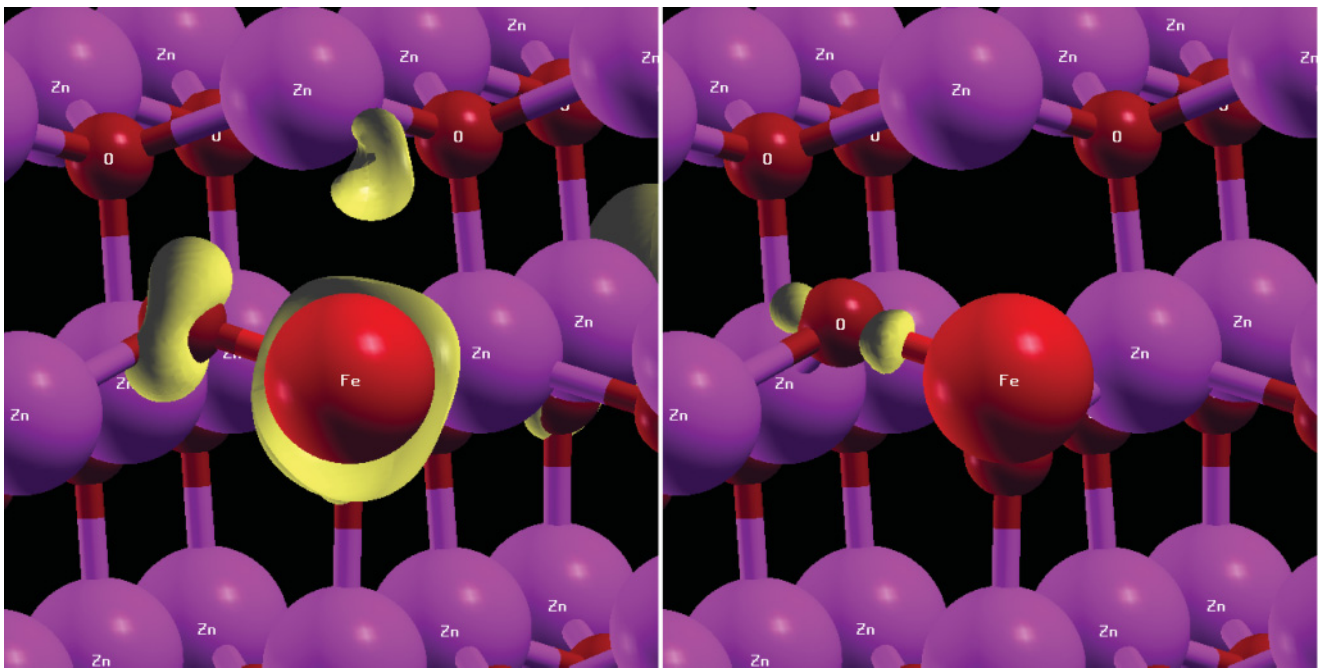

FIG. 3. (Color online) Side view of the complex Fe_{Zn}-I_O (octahedral site). In yellow are the isosurfaces for positive (0.01 a.u., left) and negative (−0.01 a.u., right) spin density.

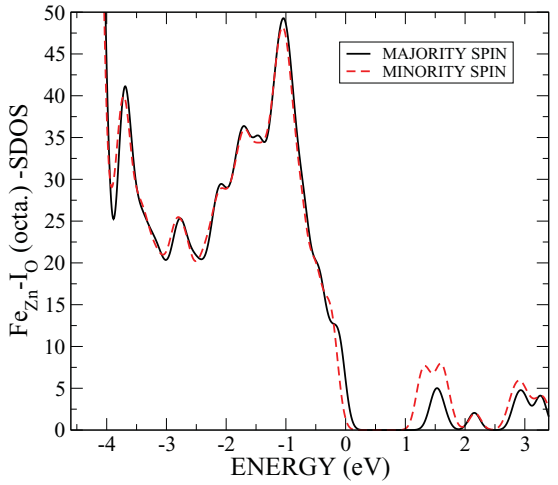

FIG. 4. (Color online) Density of state of majority and minority spin (SDOS) of ZnO with a complex formed by a substitutional Fe and an interstitial O at the octahedral site. The zero of the energy (horizontal scale) denote the Fermi energy.

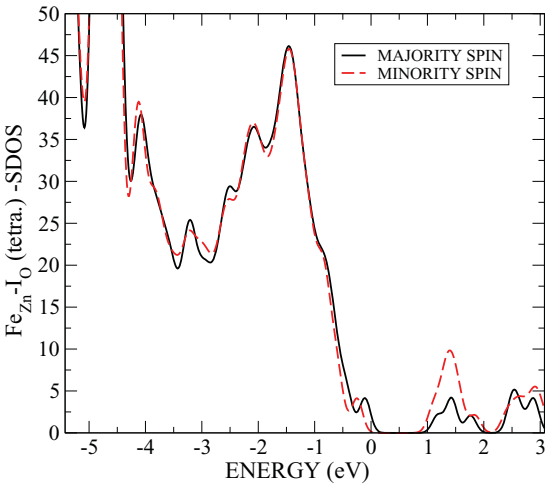

FIG. 6. (Color online) Density of state of majority and minority spin (SDOS) of ZnO doped with Fe impurity with interstitial O at the tetrahedral site. The zero of the energy (horizontal scale) denotes the Fermi energy.

total magnetization of the other tetrahedral type complex (not displayed) is $4.00\mu_B$ ($4.40\mu_B$). From Fig. 5 one can notice the ferromagnetic coupling between the Fe and the interstitial O, as well as the O surrounding the Fe_{Zn}.

In Fig. 6 we display the SDOS corresponding to the complex Fe_{Zn}-I_O (tetra) displayed in Fig. 5. The Fermi energy is almost superimposed to the valence band maximum of the minority spin, while the band edge of the majority spin is approximately a fraction of eV higher than E_F, the possibility that this complex can act as an acceptor is discussed in Sec. IV C.

We notice that the binding energy of the complexes Fe_{Zn}-I_O ranging from about 2.4 eV to about 2.9 eV (according the different configuration investigated) are considerably higher that the ones of Fe_{Zn}-V_{Zn} complexes,[18] which are ∼1.4, 1.7 eV for V_{Zn} in the fourth and in the next-nearest-neighbor shell to Fe_{Zn}, respectively. According to the suggestion of Ref. 18 the Fe_{Zn}-V_{Zn} complexes can be associated with two different complexes involving Zn vacancies that are annealed out at 400 K and 550 K.[30] Due to the larger binding energy of the complexes Fe_{Zn}-I_O, we expect these defects to be stable up to very high temperature.

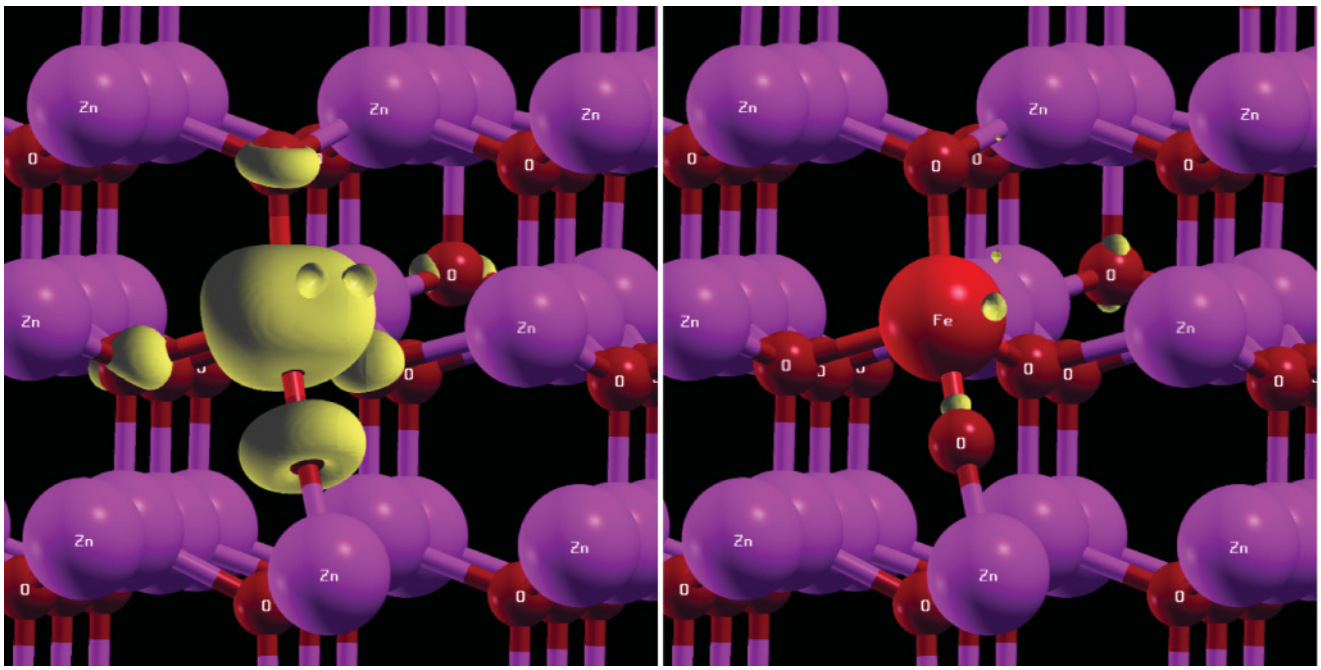

FIG. 5. (Color online) Side view of the complex Fe_{Zn}-I_O (tetrahedral site). In yellow are the isosurfaces for positive (0.01 a.u., left) and negative (−0.01 a.u., right) spin density.

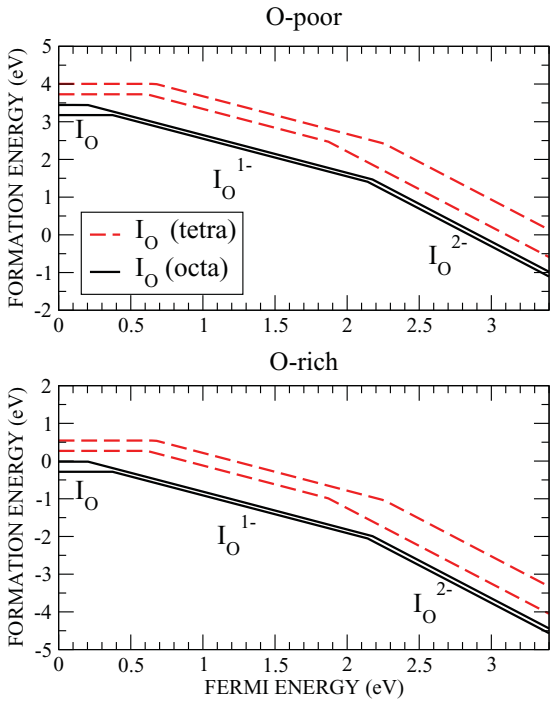

FIG. 7. (Color online) Formation energy of neutral and charged complexes Fe_{Zn}-I_O as a function of Fermi energy for O-poor (top) and O-rich (bottom) growth conditions. For each Fe_{Zn}-I_O configuration only the (charged/neutral) defect with lower energy is displayed. The zero in the vertical axis corresponds to the formation energy of Fe_{Zn}.

C. Charged complexes

According to the results displayed in Fig. 1, the complexes involving substitutional Fe and a Zn interstitial have formation energy larger than 3 eV; further, the complex with lower formation energy is the one in which Fe_{Zn} and I_{Zn} are far apart. For this reason, in studying the charged complexes, we consider only the complexes involving oxygen interstitial. In Fig. 7, we display the computed formation energy of neutral and charged complexes Fe_{Zn}-I_O as a function of the Fermi energy for O-poor (top panel) and O-rich (bottom panel) growth condition. In the same figure we also display the formation energy corresponding to the configuration in which Fe_{Zn} and I_O (tetra/octa) are far apart (in the calculation for non-neutral I_O far apart from the Fe_{Zn} we have assumed that the negative charge remains localized at the interstitial oxygen site). We computed the formation energy of the neutral and charged (with one and two electron added) Fe_{Zn}-I_O complex with the interstitial O at the octahedral and at the tetrahedral sites. For simplicity, in the figure for each complex involving O interstitial at tetrahedral or octahedral site, we display only the results for the complex (including the charged state) having the lowest formation energy. As can be noticed from the figure, the lines corresponding to the formation energies of different complexes do not intersect; that is, the complex with I_O in the octahedral position remains the one with the lowest formation energy. From the figure, we notice that at about 0.4 eV the charged complex $(1-)$ becomes stable. From these results and simple stoichiometric considerations, one can suggest that the this $(1-)$ complex presents iron in a Fe^{3+} state and the complex acts as a acceptor.

As the Fermi energy increases the complex Fe_{Zn}-I_O (octa) accepts one or two electrons end the energy difference with the other complex investigated having I_O in the octahedral site reduces. Notably, in the case of O-reach conditions, for E_F close to the bottom of the conduction band the formation energy of doubly charged Fe_{Zn}-I_O (octa) complex is more than four electron volts lower than the one of isolated Fe_{Zn}. For $E_F = 3.4$ eV (i.e., at the bottom of the conduction band) the binging energy of the Fe_{Zn}-I_O (octa) with lowest energy is 3.8 eV for O-poor and for O-rich growth conditions. The total (absolute) magnetic moments corresponding to the charged Fe_{Zn}-I_O (octa) having lowest energy among the complexes investigate are $4.92\mu_B$ $(4.97\mu_B)$ for charged defect with one electron and $4.97\mu_B$ $(5.05\mu_B)$ for charged defect with two electrons.[31]

V. CONCLUSIONS

In summary, by *ab initio* calculations we investigated the magnetic properties of isolated complexes formed in wurtzite ZnO doped with diluted Fe impurities in presence of oxygen and zinc interstitials. Our study, combined with those of Ref. 18, provide a systematic investigation of the formation energy and magnetic properties of different type of complexes formed by Fe_{Zn} and an intrinsic defect (V_{Zn}, V_O, I_O, I_{Zn}) in wurtzite ZnO. We found that for Zn-poor growth conditions the formation of Fe_{Zn}-I_O complexes is energetically favored. A similar situation was found in Ref. 18 for the complex Fe_{Zn}-V_{Zn}. Remarkably these stable complexes are the ones formed by the magnetic impurity Fe_{Zn} with one of the two intrinsic defects of ZnO (I_O and V_{Zn}) that present a spin polarization also when they are isolated, that is, far apart from other impurities. The present work suggests a possible key role of oxygen interstitial as well as of zinc vacancy[18] to enlighten the microscopic mechanisms responsible for the magnetism experimentally detected in ZnO:Fe at room temperature. The nature of the magnetic coupling between different complexes is not addressed in the present work and will be the object of future investigations.

ACKNOWLEDGMENTS

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[31]The magnetic moments are computed with a (222) MP grid to obtain a converged magnetization for the charged complexes. At variance, the qualitative behavior of the formation energies of neutral and charged complexes do not change by increasing the special points sampling to (222) MP grid.