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The current study investigates the magnetic properties of the $\text{Gd}_x\text{Zn}_{1-x}\text{O}$, with $x = 0.0625$ and 0.0185 , doped semiconductor using the full potential (linearized) augmented plane wave plus local orbital method. We show that in contrast to the findings of Shi *et al.* [J. Appl. Phys. **106**, 023910 (2009)], the implementation of the Hubbard U parameter to the Gd f states favors an antiferromagnetic phase in both wurtzite GdO and $\text{Gd}_x\text{Zn}_{1-x}\text{O}$. Spin polarized calculations on $\text{Gd}_x\text{Zn}_{1-x}\text{O}$ indicate that, even if a ferromagnetic ground state were favored, the magnetic influence of Gd in a perfect ZnO wurtzite lattice is highly localized and limited to the first three nearest neighboring O atoms. Increasing the supercell size and thus diluting the concentration of Gd within the ZnO matrix does not show any changes in the net magnetic moment between these three O atoms nor in the remaining lattice sites, indicating that sizing effects do not influence the range of matrix polarization. We conclude that the localized Gd induced polarization can not account for long range magnetic ordering in a defect-free ZnO wurtzite lattice. © 2011 American Institute of Physics. [doi:10.1063/1.3574924]

I. INTRODUCTION

The search for room temperature magnetic semiconductors has opened promising directions in the development of semiconductor-based spintronics.¹ A large number of experimental and theoretical studies have been realized to achieve room temperature ferromagnetism while preserving the semiconductor properties of the material. From this perspective, the theoretical analysis proposed by Dietl *et al.*^{2,3} has long served as a roadmap in the exploration of ferromagnetic semiconductors. Whereas the most widely used diluted magnetic semiconductor (DMS), $(\text{Ga,Mn})\text{As}$, has a highest reported Curie temperature of 185 K,⁴ alternative materials such as Co-doped TiO_2 (Ref. 5) and ZnO ,⁶ Mn-doped ZnO (Refs. 7 and 8) and GaN,⁹ and C-doped ZnO (Refs. 10 and 11) also proved to display room temperature ferromagnetism.

Theoretically, most of the materials that have been studied are semiconductors doped with partially filled $3d$ state transition metals (TMs). Because of the strong coupling between the magnetic ions' $3d$ states and the coupling to the host p states, diluted magnetic nitride and oxide semiconductors have been predicted and, in some cases, observed to show hole-mediated ferromagnetic behavior above room temperatures.^{12,13} These calculations showed also that V-, Mn-, and Cr-doped GaN are promising candidates as room temperature ferromagnetic semiconductors and that Cr-doped GaN has the most stable ferromagnetic states.

In the area of rare-earth (RE) doped semiconductors, a theoretical study by first-principles calculation was performed for $\text{Ga}_{1-x}\text{Gd}_x\text{N}$ ($x = 0.25$).¹⁴ The authors showed that the interactions between Gd atoms in undoped $\text{Ga}_{1-x}\text{Gd}_x\text{N}$ are antiferromagnetic in nature but can become ferromagnetic by introducing donors in the material. Moreover, in contrast with most $3d$ DMSs, ferromagnetism in $\text{Ga}_{1-x}\text{Gd}_x\text{N}$ is electron mediated. Although $4f$ orbitals are more localized, resulting in a weak direct coupling between the magnetic

ions, $4f$ RE elements can have larger magnetic moments than the $3d$ elements. Therefore, unlike the d states, f electrons can couple strongly with the host s electrons, leading to the possibility of electron-mediated ferromagnetism in these materials. The fabrication of electron-mediated DMSs together with hole-mediated DMSs offers interesting opportunities for bipolar magnetic semiconductor devices.

Among the materials considered as potential DMS candidates, ZnO is well known for its piezo-electric and electro-optical properties. Magnetic ZnO would then provide a flexible multifunctional material for spintronics applications. Magnetism in pure ZnO has been observed experimentally and the role of oxygen vacancies and defects has been pointed out.^{15–17} Alternatively, doping by magnetic impurities such as transition or rare-earth metals has been explored in order to achieve large saturation magnetization. For example, Mn-doped ZnO has been shown to display ferromagnetism, mediated by holes.^{7,8} On the other hand, the doping by donors, rather than acceptors would allow to obtain n -type DMS that could be used as a building block for bipolar semiconductor devices such as p - n junctions, as mentioned above.

From this point of view, doping with Gd yielded promising results in GaN matrices^{18,19} and is expected to generate ferromagnetic order in ZnO.²⁰ However, the experimental results obtained to date on Gd-doped ZnO are still controversial and seem highly dependent on the doping procedure.^{21–23} Only few theoretical studies²⁰ exist on this system and a deep understanding of the physical mechanisms responsible for the ferromagnetism is needed to achieve decisive progress. For instance, the polarization of the host matrix in Gd atoms, as observed in GdGaN ,¹⁸ has not been confirmed in GdZnO .

To get a deep understanding of the electronic and magnetic properties in the RE doped systems, we have performed total energy calculations on $\text{Zn}_{1-x}\text{Gd}_x\text{O}$. We find that the commonly applied generalized gradient approximation (GGA) is not sufficient to describe this system and one must

account for on-site electron-electron interactions using the GGA+U method. Within this framework, we show that the Gd impurities induce a spin polarization of their environment that rapidly decays away from the Gd atoms.

The paper is organized as follows. Computational details are presented in Sec. II. Section III is devoted to the electronic properties in terms of the density of states (DOS) and the discussion of supercell size effects. In Sec. IV, we present our calculated magnetic properties. The paper ends with the main conclusions about the electronic structure and magnetism of $\text{Gd}_x\text{Zn}_{1-x}\text{O}$, Sec. V.

II. COMPUTATIONAL DETAILS

Ab initio spin-polarized all-electron density functional theory calculations have been performed for substitutional gadolinium (Gd) in zinc oxide (ZnO), using the GGA approximation of Perdew-Burke-Ernzerhof²⁴ for the exchange-correlation functional. The linearized augmented plane wave method with local orbitals basis set was employed using the full potential periodic formalism with relativistic treatment of the core²⁵ and valence²⁶ electrons, as implemented in the WIEN2k code.²⁷ Blöchl's modified tetrahedron method²⁸ was used for integration over the Brillouin zone. The following initial atomic configurations were employed: $4f^7 5d^1 s^2$ (Gd), $3d^{10} 4s^2$ (Zn), and $2s^2 2p^4$ (O). All the $\text{Gd}_x\text{Zn}_{1-x}\text{O}$ calculations were spin polarized. The muffin-tin radii are considered to be equal to 1.97, 1.97, and 1.74 Bohr units for Gd, Zn, and O atoms, respectively. For the GGA+U method, we use the scheme introduced by Anisimov *et al.*²⁹ with an approximate correction for the self-interaction correction. This is probably best suited for our system and for a full potential method we use an effective $U_{\text{eff}} = U - J$, setting $J = 0.5$ and $U = 7.4$ eV, for Gd and consider two values of U for Zn, $U_{\text{eff}} = 4.7$ eV and 8.5 eV quoted from Refs. 30 and 31, respectively. The self consistent procedure has been carried out with the energy cutoff constant $R_{\text{MT}}K_{\text{max}} = 8$ and the Brillouin zone integrations were performed with the special k -points method over $9 \times 9 \times 5$ Monkhorst-Pack mesh.³² The convergence has been followed with respect to the energy and the density.

Experimentally determined lattice constants of pure ZnO in wurtzite structure were used in the calculation,³³ with $a = 3.249$ Å, $c = 5.200$ Å and $u = 0.345$. The calculated lattice parameters a and c are 3.28 Å and 5.30 Å, respectively. The deviations from experimental values were overestimated for both quantities by 1% and 1.7%, respectively. We have also calculated the structural parameters of hypothetical GdO in wurtzite and zinc blende phases. Our predicted lattice parameters a and c are 3.28 Å and 5.30 Å. Interestingly, total energy calculations show that undoped GdO in the wurtzite and zinc blende phases are more stable in the antiferromagnetic phase: the energy difference between ferromagnetic (FM) and antiferromagnetic (AFM) phases are 11.7 meV. Notice that this contradicts with the results reported in Ref. 20. This discrepancy can be attributed to the influence of electron-electron interaction as accounted for in GGA+U approximation.

To build $\text{Gd}_x\text{Zn}_{1-x}\text{O}$ structures, we considered two supercells composed of $2 \times 2 \times 2$ and $3 \times 3 \times 3$ unit cells

FIG. 1. Illustration of a $2 \times 2 \times 2$ wurtzite-ZnO supercell displaying a Gd atom in a Zn site.

of wurtzite ZnO, containing, respectively, 32 and 108 atoms. Refer to Fig. 1 for an illustration of the $2 \times 2 \times 2$ supercell. In each supercell, a Zn atom was substituted by one Gd impurity, in order to obtain $\text{Gd}_x\text{Zn}_{1-x}\text{O}$ with $x = 0.0625$ and 0.0185. We first performed our calculation for the FM and AFM phases and found both to be energetically stable, with the AFM lower in energy by 9.7 meV than the FM configuration. However, the energy differences between the FM and AFM states are small when compared with TM doped ZnO, an observation explained by the highly localized character of the f orbitals.

III. ELECTRONIC STRUCTURE

In order to understand the effect of Gd substitution in wurtzite ZnO, we start our calculations by a preliminary study of bulk binary materials. We have calculated the spin

FIG. 2. Total and partial density of states of ferromagnetic GdO in the hypothetical wurtzite structure calculated by both the GGA (lower panel) and GGA+U (upper panel) schemes. The vertical solid line denotes the Fermi level.

polarized total and partial density of states of the hypothetical GdO which crystallizes in the wurtzite structure using both GGA and GGA+U approximations, see Fig. 2. Due to the highly localized character of the f states, the GGA approximation cannot accurately describe the strong correlations in the system. It is necessary to introduce the Coulomb repulsion parameter U in order to overcome the drawback mentioned above. The GGA+U method has been used with considerable success in the description of electronic structure and magnetism.^{34–36} From Fig. 2, we show that the application of GGA+U induces changes to the f levels compared to GGA. Furthermore, we show from the figure that the majority spin $4f$ states are fully occupied around -9 eV and are located below the oxygen p states. The minority spin $4f$ states are fully unoccupied and are nearly 3 eV above the Fermi level. This is comparable to the GdN case, in which the majority spin $4f$ are below the nitrogen p states.³⁷ Contrary to what has been reported in a recent paper²⁰ on zinc blende GdO, where the authors attest that the application of U parameter will not affect very much the electronic description, we find that the application of GGA+U modifies the density of state, i.e. mainly the position of the f states. In the present work, we note also that the Gd s states are located below the Fermi level in both majority and minority spin states.

The DOS calculated in ferromagnetic configuration for $x=0.0185$ and $x=0.0625$ in $\text{Gd}_x\text{Zn}_{1-x}\text{O}$ are plotted in Fig. 3(a). They appear to be very similar. The DOS figures clearly show that when a Gd atom is incorporated into ZnO, it introduces new states inside the valence band (for the DOS of pure ZnO please refer to Fig. 10 in the review by Özgür *et al.*³⁸). We also notice that the general features are the same as in pure GdO. The partial densities of states are presented in Fig. 3(b), showing several interesting features. It is found that in the majority spin, Gd $4f$ states are always inserted below Fermi level around -10 eV, whereas in the minority spin Gd $4f$ states are about 5 eV above the Fermi level. We must note here that our results are in disagreement with the calculations reported in Ref. 20, essentially regarding the location of the $4f$ states in majority spin (about -20 eV). It is also important to note that for the Gd doped ZnO, the $4f$ states can couple strongly with the host s states. Moreover, the s - f coupling is much larger than the f - f and f - p couplings, which suggests possible electron mediated ferromagnetism in this system.

IV. MAGNETISM

The data in Table I displays magnetic moments (MMs) obtained from two different supercells of zinc oxide for four separate cases for the application of the Hubbard U parameter. Calculations for each cell size were repeated with four different combinations of the Hubbard U parameter for the three atoms (O, Zn, and Gd) to correct for the strong Coulomb interaction. For example, contradictory to experimental observation, calculations using the localized spin density approximation (LSDA) predict bulk hcp Gd to have an AFM ground state.^{39,40} A stable FM solution can be obtained by implementing the LSDA+ U method to the localized Gd $4f$

FIG. 3. Calculated total density of states for ferromagnetic $\text{Gd}_1\text{Zn}_{15}\text{O}_{16}$ and $\text{Gd}_1\text{Zn}_{53}\text{O}_{54}$ supercells for majority (upper part) and minority (lower part) spin states.

states.⁴¹ Similarly, considering the on-site Coulomb interaction U for the Zn $3d$ states can influence the bonding mechanism³¹ and bandgap in ZnO.³⁰

The influence of the U parameter on the values of magnetic moment in the Gd atom (MM_{Gd}) is shown in Table I. Employing $U = 6.9$ eV to Gd increases MM_{Gd} by 0.125 and

TABLE I. Table of magnetic moments (MM_{Gd} and MM_{latt}) for different cell sizes and values of the Hubbard U parameter applied to the Zn d and Gd f orbitals, with U quoted in eV.

		Case 1	Case 2	Case 3	Case 4
Cell		$U_{eff}^{All} = 0.0$	$U_{Gd}^{Gd} = 6.9$ $U_{Zn}^{Zn} = 0.0$	$U_{Gd}^{Gd} = 6.9$ $U_{Zn}^{Zn} = 4.7$	$U_{Gd}^{Gd} = 6.9$ $U_{Zn}^{Zn} = 8.5$
$2 \times 2 \times 2$	MM_{Gd}	$6.712 \mu_B$	$6.837 \mu_B$	$6.837 \mu_B$	$6.837 \mu_B$
	MM_{latt}	$0.000 \mu_B$	$-0.019 \mu_B$	$-0.020 \mu_B$	$-0.021 \mu_B$
$3 \times 3 \times 3$	MM_{Gd}	$6.719 \mu_B$	$6.838 \mu_B$	$6.838 \mu_B$	$6.838 \mu_B$
	MM_{latt}	$-0.001 \mu_B$	$-0.019 \mu_B$	$-0.021 \mu_B$	$-0.022 \mu_B$

$0.119 \mu_B$ for the $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells, respectively, compare Case 1 and 2 in Table I. This increase is due to a shift of the majority Gd f states to lower energy levels, Gd f graph in Fig. 4. As these states now occupy lower energies they will find themselves closer to the Gd atom core and thus further from the muffin-tin boundary. In turn, f electron charge is removed from the interstitial region. It is worth noting that, in support of the above argument, the increase in MM_{Gd} is accompanied with a decrease in MM in the interstitial region of the cell. Employing U to Zn atoms results in no further change to MM_{Gd} for both supercell sizes, compare Case 2 with that of 3 and 4 in Table I.

FIG. 4. Partial density of states for the Gd f, d, and s states in the $3 \times 3 \times 3$ supercell comparing Case 1 (dashed line) and Case 2 (solid line), refer to Table I.

Changes in the net induced MM over the rest of the host lattice (MM_{latt}), i.e., all atoms excluding Gd, with the application of the U parameter are also displayed in Table I. Calculations performed without U reveal MM_{latt} near to zero for both the $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells. Implementing $U = 6.9$ eV to the Gd atom increases the magnitude of MM_{latt} by 0.019 and $0.018 \mu_B$ in the $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells, respectively, compare Case 1 and 2. The application of $U = 4.7$ eV to the Zn atoms increases the magnitude of MM_{latt} by $0.001 \mu_B$ for the $2 \times 2 \times 2$ supercell and $0.002 \mu_B$ for that of the $3 \times 3 \times 3$, Case 2 and 3. Increasing U for Zn to 8.5 eV further increases the magnitude of MM_{latt} by $0.001 \mu_B$ for both supercell sizes, Case 3 and 4. Table I indicates that the treatment of the Gd f states plays a larger role on the influence of the U parameter on MM_{latt} than the Zn d states.

The observed increase in MM_{latt} with the application of U to Gd is accounted for by the shifting of the occupied f

FIG. 5. Graph of magnetic moment as a function of distance from the Gd atom. Data is displayed for the $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells comparing $U_{eff} = 0.0$ and 7.3 eV applied to Gd f states.

FIG. 6. (Color online) Spin density contour plot from the $2 \times 2 \times 2$ supercell, refer to Fig. 1 for atom positions in lattice.

states, see Fig. 4. This shifting to lower energies, coupled with the narrowing of the Gd f band makes the f states more localized. Consequently the Coulomb attraction between the atom core and the $5d$ and $6s$ valence states is reduced, reducing the available states at particular energies (Gd d and s peaks in Fig. 4) and distributing these states more evenly across their respective energy range. The delocalization of the d and s states allows them to interact and further polarize the neighboring oxygen atoms, illustrated by the increase in MM in the two nearest neighbors to Gd with the implementation of $U_{\text{eff}}^{\text{Gd}}$, see Fig. 5.

Despite this increase in the magnitude of MM within neighboring atoms, values of MM rapidly converge to zero. Atoms at distances greater than ~ 4.0 Å (i.e., after the first three nearest neighbors to Gd) do not contribute to the total magnetic moment in the cell ($\text{MM} < 10^{-3} \mu_B$), Fig. 5. Illustrating that the magnetic influence of Gd in the ZnO matrix is highly localized.

Further evidence of the highly localized influence of Gd can be seen when observing the MM distribution near the Gd atom in the ZnO lattice. Figure 6 displays a two-dimensional mapping of the spin densities for the $2 \times 2 \times 2$ supercell. Spin density is estimated as the difference between the majority and minority electron densities. The figure shows that the main moments in the cell arise from Gd atoms. Consistent with the above description, the O atoms being the nearest neighbors of Gd atoms possess the largest Gd-induced polarization, with a negative contribution to the total moments, whereas the Zn atoms contribute with a small positive moment.

Figure 7 shows a plot of spin density versus distance for atoms lying along the c -axis of the $\{10\bar{1}0\}$ crystal plane intersecting one Gd atom. Atoms displayed are Gd16, O8, O4, and Zn14 from the $2 \times 2 \times 2$ supercell. The figure has been scaled and displayed over a schematic of the crystal structure for ease of reference between atoms and peaks.

It is worth noting four points from the graph in Fig. 7. First, that there is a high density of magnetically uncoupled

FIG. 7. Plot of spin density as a function of distance along the c -axis of the $\{10\bar{1}0\}$ plane. Includes a schematic of the $2 \times 2 \times 2$ ZnO supercell viewed perpendicular to the $\{10\bar{1}0\}$ plane.

electrons in the vicinity of the Gd16 atom. The spin density spans a distance of around 2.0 Å and has maximum intensity at approximately -150 electron per Å.³ This value is three orders of magnitude higher than the absolute value of the second most intense peak, that of O8. Second, that the Zn atoms have a spin density close to zero and hence do not appear to be magnetically influenced by the presence of Gd. Third, that the nearest atom to Gd16 along the c -axis is O8 which also shows the highest degree of polarization,

FIG. 8. Schematic showing the four neighboring oxygen atoms to gadolinium which contribute to the total magnetisation per cell. Arrows indicate the spin polarity of each oxygen atom.

approximately $+0.15$ electron per Å,³ but is of opposite polarity to its Gd16 neighbor. Finally, even though the magnitude of spin density in the O4 atom is only about one fifteenth that of O8 and it does not share a direct bond with Gd16 it shares a similar polarity.

In light of this one may see that it is an increase in the polarization of atom O4 and a decrease in O8 that will contribute to increasing MM_{tot} in the supercell beyond that of the single contribution from Gd16. This is true when considering the one-dimensional case along the *c*-axis of the supercell, but in the three-dimensional situation one has to also include atom O3 which has a multiplicity of three due to symmetry about the *c*-axis. Figure 8 is a schematic depicting the five O atoms that have the most influence on the MM per cell (O8, O4, and three O3 atoms).

Arrows within the O atoms in Fig. 8 indicate the direction of spin within each atom, spin-up ($\uparrow$) and spin-down ($\downarrow$). Between the O atoms of this configuration there is a spin majority MM of $0.038 \mu_B$ and a spin minority of $0.003 \mu_B$. Leading to a net spin-up MM of $0.035 \mu_B$. An increase in supercell size from $2 \times 2 \times 2$ to $3 \times 3 \times 3$ and hence a decrease in the ratio of Gd to Zn from 1 in 16 atoms to 1 in 54 does not change the shared net MM between these atoms. Investigating the MM of atoms in other sites of the matrix show that they have MM values equivalent to those of the pure ZnO unit cell ($MM < 10^{-3} \mu_B$), see MM values at distances greater than $4.0 \text{ \AA}$ in Fig. 5. Hence, the magnetic influence of Gd when substituting Zn in a perfect wurtzite ZnO lattice is confined to the five O nearest neighbor atoms and does not show any sizing effects related to the number of atoms in the supercell.

V. CONCLUSION

In the present study, we have performed *ab initio* density functional theory calculations to investigate the range of magnetic ordering in a defect-free wurtzite ZnO lattice induced by the presence of Gd impurities. Emphasis is placed on the implementation of the Hubbard *U* parameter to account for the Coulomb interaction of the highly localized Gd *f* states ($U_{\text{eff}} = U - J = 6.9 \text{ eV}$). From our calculations we observe the following:

- When accounting for the localized Gd *f* states, both wurtzite GdO and $Gd_xZn_{1-x}O$ (with $x = 0.0625$ and 0.0185) favor an antiferromagnetic phase.
- Application of the GGA+*U* method to the Gd *f* states increases the total magnetic moment in the supercell, MM_{tot} , due to the effective delocalization of the Gd *5d* and *6s* states. Further application of *U* to account for the Zn *d* states shows little change in MM_{tot} .
- The range of matrix polarization due to Gd additions is very small, limited to O atoms that lie within $4.0 \text{ \AA}$ of the impurity with the remaining atoms in the lattice displaying magnetic moment values comparable to those of pure ZnO.
- Increasing the supercell size and thus diluting the concentration of Gd in the matrix shows no further increase in the net magnetic moment due to the mentioned oxygen atoms nor in the residual lattice sites.

It is thus concluded that additions of Gd to a defect-free ZnO wurtzite lattice do not show any long range ferromagnetic ordering when accounting for the correlations of the Gd *f* states.

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