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Ferromagnetism in Gd doped ZnO nanowires: A first principles study

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In several experimental studies, room temperature ferromagnetism in Gd-doped ZnO nanostructures has been achieved. However, the mechanism and the origin of the ferromagnetism remain controversial. We investigate the structural, magnetic, and electronic properties of Zn₄₈O₄₈ nanowires doped with Gd, using density functional theory. Our findings indicate that substitutionally incorporated Gd atoms prefer occupying the surface Zn sites. Moreover, the formation energy increases with the distance between Gd atoms, signifying that no Gd-Gd segregation occurs in the nanowires within the concentration limit of $\leq 2\%$. Gd induces ferromagnetism in ZnO nanowires with magnetic coupling energy up to 21 meV in the neutral state, which increases with additional electron and O vacancy, revealing the role of carriers in magnetic exchange. The potential for achieving room temperature ferromagnetism and high T_C in ZnO:Gd nanowires is evident from the large ferromagnetic coupling energy (200 meV) obtained with the O vacancy. Density of states shows that Fermi level overlaps with Gd f states with the introduction of O vacancy, indicating the possibility of s - f coupling. These results will assist in understanding experimental findings in Gd-doped ZnO nanowires. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4904860>]

I. INTRODUCTION

Recent years have witnessed a renewed research interest in ZnO due to its potential applications in optoelectronics, photochemical cells, diluted magnetic semiconductors (DMS), field effect transistors, and photoluminescent devices, to name a few.¹⁻⁴ In searching for room temperature ferromagnetism (RTFM) in ZnO, transition metal (TM) doping is widely investigated.⁵ Recently, the focus has shifted to rare-earth (RE) dopants, aiming to invoke magnetic coupling in ZnO by induced spin polarization. A few theoretical studies have reported weak FM in RE-doped bulk ZnO in zincblende and wurtzite structures.⁶⁻⁸ Even though the $4f$ levels are localized in RE elements, f electrons can couple strongly with host s electrons,⁶ yielding the possibility of carrier-mediated FM.⁷ In particular, the interest in ZnO nanostructures has significantly increased in recent years owing to their unique optical, magnetic, and mechanical properties, leading to many potential applications. However, the mechanism and the origin of the ferromagnetism remain controversial. Assadi *et al.*⁷ have found that Eu ions doped into ZnO couple ferromagnetically when they are in nearest neighbor positions. While the same applies to Gd doping, the observed ferromagnetic coupling depends on the crystal structure and positions of the dopant atoms in the host matrix, as well as the distance between RE dopants.⁸ FM is observed experimentally in ZnO thin films^{9,10} and ZnO nanostructures doped with RE elements, such as Eu, Nd, and Gd.^{11,12} In several experiments on ZnO nanowires doped with Gd, huge magnetic moments ($3278\mu_B/\text{Gd}$) were obtained, which is attributed to the exchange interaction between $4f$ and $6s$ electrons.¹¹ Nd-doped ZnO nanowire arrays exhibit stable RTFM with magnetic

moments of $4.1\mu_B/\text{Nd}$.¹² Gd-implanted ZnO single crystals¹³ showed saturation moments of up to $1.8\mu_B/\text{Gd}$ and FM has also been reported in nano-crystalline ZnO doped with 3.5% Gd.¹⁴ However, it has been noted that a high concentration of Gd impurities in ZnO thin films leads to paramagnetism.¹⁵

In this scenario, doping with Gd seems to be a promising way to achieve RTFM in ZnO nanostructures. However, the existing experimental results are controversial and depend strongly on the doping method and the defect type.^{10-12,15} In addition, the mechanism and origin of the magnetic coupling are poorly understood. The few theoretical studies that have been conducted thus far deal with RE doping in bulk ZnO and do not elucidate the mechanisms responsible for RTFM in Gd-doped wurtzite ZnO nanostructures.⁶⁻⁸ On the other hand, it is important to understand the physical mechanisms responsible for the FM in ZnO nanostructures from both fundamental and technological perspectives. In this paper, we demonstrate FM in Gd-doped Zn₄₈O₄₈ nanowires oriented along the wurtzite [0001] direction, as well as the effect of point defects on the magnetic coupling, using first-principles calculations. As it is not computationally feasible to model nanostructures beyond a few nanometers, density functional theory (DFT) studies are often conducted on nanowires of diameters ranging from sub-nanometer to ≤ 3 nm in order to study the properties of nanowires and allow comparisons with experimental findings.^{16,17} In particular, nanowires of diameter ranging from 1.6 to 5 nm can now be fabricated by experimental techniques.¹⁸ In addition, DFT studies on nanowires of diameter less than 1 nm assist in understanding the optical properties due to the presence of quantum size effects that generally result in substantial density of states (DOSs) at the band edge.¹⁷ The diameter of the wurtzite ZnO nanowire in the present study is about 1 nm, which is sufficient for examining the relative stability and segregation of Gd, in the

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dilute limit. In order to advance the understanding of the magnetic mechanism, we also investigate the electronic structure of these nanowires.

II. COMPUTATIONAL METHODOLOGY

In this work, a $\text{Zn}_{48}\text{O}_{48}$ nanowire of about 1 nm diameter, oriented along wurtzite [0001] direction is modeled using the supercell approach. A vacuum of 15 Å thickness is created along X and Y directions to ensure that the interaction between the nanowire and its periodic images remains negligible. The supercell has a length of $2c$, where c is the bulk lattice parameter along the [0001] direction, such that it contains 96 atoms ($\text{Zn}_{48}\text{O}_{48}$). We employ the Vienna *Ab initio* Simulation Package (VASP)¹⁹ to carry out our spin-polarized first-principles simulations, using the generalized gradient approximation (GGA)²⁰ and plane wave cut-off energy of 400 eV. Methods such as GGA+U and Self-Interaction Corrected LDA (SIC-LDA)²¹ are widely used to treat ZnO-based systems, as this allows overcoming the “band-gap” problem. A comparison of the results pertaining to LDA and LDA+U in $\text{ZnO}:\text{Gd}$ systems showed that the qualitative picture is mostly unchanged, with the exception of some quantitative changes.^{6,22,23} Hence, we do not expect the main trend of electron-mediated FM described in our paper to be altered significantly if Hubbard U correction or SIC-LDA is taken into account. The pseudopotentials are based on the projector augmented wave formalism.²⁴ The Brillouin zone sampling is carried out in the Monkhorst-Pack scheme using a $1 \times 1 \times 8$ mesh. The atomic coordinates are allowed to relax without geometry and spin constraints. Energy and force tolerances of 0.0001 eV and 0.004 eV/Å, respectively, are achieved.

The Gd atoms are incorporated into $\text{Zn}_{48}\text{O}_{48}$ nanowires at substitutional Zn sites, which are favored by RE elements.⁸ To determine the preferred Gd positions, total energy calculations are performed for 12 configurations, divided into 3 groups, encompassing surface, sub-surface, and bulk-like regions, as shown in Fig. 1 (groups 1, 2, and 3, respectively). These calculations are conducted on

freestanding nanowires without surface passivation. The formation energy (E^f) of Gd is calculated as

$$E^f = E(\text{Zn}_{48-m}\text{O}_{48}\text{Gd}_m) - E(\text{Zn}_{48}\text{O}_{48}) + n\mu(\text{Zn}) - m\mu(\text{Gd}), \quad (1)$$

where E and μ represent the total energy and chemical potential (total energy of metallic Zn and Gd), respectively. Here, n is the number of Zn atoms removed from the supercell and m denotes the number of Gd atoms substituted to the Zn sites.

III. RESULTS AND DISCUSSION

We first optimize the internal coordinates of the atoms in the nanowires without dopant. The relaxation of atomic coordinates is important in the pristine nanowire, due to the large surface area/volume ratio. We find that the relaxation of the surface atoms is larger than that of the inner atoms. In bulk wurtzite ZnO, the Zn-O bond length is 1.99 Å. For the relaxed nanowire, this bond length becomes 1.89 Å in the c -direction, while it is 2.06 Å in the ab -plane. Therefore, after optimization, the nanowires have distortion along the c -axis, compared to the bulk.

One Gd atom is substitutionally incorporated to the Zn site in the $\text{Zn}_{48}\text{O}_{48}$ nanowire (corresponding to a doping concentration of about 1%) and relaxation is carried out without any geometry or spin constraints. We consider all symmetrically non-equivalent substitutional sites, as shown in Fig. 1. We find that the Gd-O bond length along the c -direction changes from 1.89 Å to 2.08 Å, while the change within the ab -plane is negligible (0.01 Å). Hence, the $\text{Zn}_{47}\text{O}_{48}\text{Gd}$ nanowires reach structural stability with less pronounced lattice distortion. The calculated E^f of Gd atoms in the $\text{Zn}_{47}\text{O}_{48}\text{Gd}$ nanowires is also given in Fig. 1. The formation energy in the neutral state determines the solubility in the host matrix, with a high value indicating low solubility.

The lowest value of E^f (favorable position) is obtained when the Gd atom is located on the surface of the nanowire (group 1c). Correspondingly, the value of E^f increases as the Gd location shifts towards the bulk-like region. This preference of the surface sites is in line with the experimental

FIG. 1. $\text{Zn}_{47}\text{O}_{48}\text{Gd}$ nanowire configurations with one Zn atom replaced by Gd. The 12 configurations are divided into 3 groups for all non-equivalent substitutional sites. The energy (in eV) is denoted for each configuration.

findings in which RE dopants accumulate on the surface of ZnO nanowires during *in situ* deposition.¹¹ We find that an isolated Gd atom incorporated in a Zn site exhibits a magnetic moment of about $6.87\mu_B$, for all Gd positions.

Increasing the Gd concentration will provide insight into the energetic preference, as well as about the Gd-Gd interaction, and allow us to gain better understanding of the potential for RTFM. For this purpose, we incorporate two Gd atoms into the $\text{Zn}_{48}\text{O}_{48}$ nanowire (Gd concentration of about 2%), considering different configurations of substitutional sites in the surface, sub-surface, and bulk-like regions. In addition, for each Gd-Gd distance, several spatial arrangements are considered. The E^f for all configurations is calculated using Eq. (1). Fig. 2 shows E^f as a function of Gd-Gd distance in $\text{Zn}_{46}\text{O}_{48}\text{Gd}_2$ nanowire. As the Gd atoms prefer the surface substitutional Zn sites, we examine possible surface configurations and for comparison, the sub-surface and bulk-like regions. We obtain the lowest values of E^f for the surface configurations. Interestingly, for similar Gd-Gd distances, E^f is lower at the surface than in the bulk-like region. In addition, Gd atoms prefer to stay away from each other (as shown in Fig. 2), indicating that no Gd segregation can occur for Gd-doped ZnO nanowire in the low concentration limit of this study. This finding implies that magnetism observed in ZnO nanostructures with low RE concentration (2%, i.e., below the solubility limit) may not be due to Gd clusters. On the other hand, extant experimental studies have reported clustering tendency at higher RE concentrations (>2.5%) in ZnO.²⁵ Several studies indicate that ZnO doped with TMs often suffers from the magnetic percolation problem at impurity concentrations of about 5%–10%, due to short-ranged exchange interactions. Therefore, obtaining high T_C in ZnO doped with RE and TM is difficult due to the magnetic percolation issues.²⁶ In this case, if the doped ZnO undergoes spinodal decomposition, due to the attractive interaction between magnetic clusters, magnetic percolation paths can be formed, leading to superparamagnetism, as a result of the strong magnetic coupling between atoms in the same cluster. If the impurity cluster is sufficiently large, the relaxation time required to flip the magnetization becomes

FIG. 2. The formation energy of Gd atoms in $\text{Zn}_{46}\text{O}_{48}\text{Gd}_2$ nanowires as a function of the separation between two Gd atoms.

rather long, enhancing the blocking temperature. However, the Gd concentrations considered in the present study ($\leq 2\%$) are too low to observe magnetic percolation effects.²⁷

We investigate the possibility of exchange coupling between Gd atoms by calculating the energy difference (ΔE) between ferromagnetic and antiferromagnetic (AFM) (as shown in Table I and Fig. 3) configurations. In Figs. 3(a)–3(d), some selected configurations for different Gd substitutional sites on the surface are shown. These configurations can be contrasted with Figs. 3(e)–3(g), which show the nanowire configurations in which Gd atoms are substituted in the bulk-like region of the nanowire. We show this comparison because it has been reported that, during RE ion implantation into ZnO, the dopant atoms are distributed homogeneously.²⁸

We find that ΔE is sufficiently large in favor of FM coupling in Gd-doped ZnO nanowires in the neutral state. A significant ΔE (as high as 21 meV) is obtained for the nearest neighbor Gd atoms in the neutral state. However, the ΔE value decreases to 4 meV as the distance between Gd dopants increases (in defect-free $\text{Zn}_{46}\text{O}_{48}\text{Gd}_2$ nanowire), as shown in the second column of Table I. Furthermore, we investigate the effects of additional charge injected into the nanowires. According to our findings, introduction of one electron clearly enhances the FM, as can be seen in the third column of Table I. We also introduce intrinsic point defects, such as Zn vacancy (V_{Zn}) and O vacancy (V_{O}). It has been shown previously that V_{O} has the lowest E^f among the native donor defects in ZnO.²⁹ The location of V_{O} in each nanowire configuration is indicated in Fig. 3. We find that V_{Zn} does not enhance the FM, whereas V_{O} has a drastic effect, much stronger than the additional charge (see the fourth column of Table I). This phenomenon is due to the fact that, one V_{O} introduces two electrons and leads the system to a more stable FM state. In the presence of V_{O} , ΔE is significantly larger (200 meV) than that measured for a defect-free ZnO nanowire. Hence, long-range FM can be achieved when the Gd-Gd distance is maintained within 6 Å. This is in line with extended x-ray absorption fine structure measurements; RE dopants are found to be incorporated into ZnO nanowires at distances below 5 Å.²⁵ The observed effects of the additional charge and V_{O} support the premise that the FM is due to *f-s* coupling. Experimental findings show that FM due to electron-mediated exchange is observed in n-type ZnO,³⁰ in line with our calculated results. However, our findings

TABLE I. Total energy difference between FM and AFM configurations, for the $\text{Zn}_{46}\text{O}_{48}\text{Gd}_2$ nanowires shown in Fig. 3 without defects (second column) and with the introduction of electron (e) (third column) and V_{O} (fourth column).

Configuration	ΔE (meV)	ΔE (e) (meV)	ΔE (V_{O}) (meV)
a	4	20	31
b	11	35	96
c	21	57	134
d	9	23	108
e	17	86	200
f	13	21	60
g	9	14	46

FIG. 3. Different configurations of $\text{Zn}_{46}\text{O}_{48}\text{Gd}_2$ nanowires with two Zn atoms replaced by Gd. The total energy differences between FM and AFM for each configuration are shown. The V_O positions are indicated by green spheres. Note that the FM coupling varies with the distance and location of Gd atoms in the nanowire.

suggest that RTFM can be stabilized in $\text{ZnO}:\text{Gd}$ nanowires, by electrons and V_O , as FM is favored with a significant energy gain ($\Delta E > 30 \text{ meV}$), which is sufficient to establish RTFM. This confirms that superparamagnetic phase cannot be occurred in these nanowires. In this study, we show that, due to the strong localized nature of the $4f$ electrons, carriers are required to establish ferromagnetic exchange in RE-doped ZnO. On the other hand, in the case of TM-based ZnO materials, FM can be stabilized with or without carriers.^{30,31} The large ΔE obtained in our investigation is an indication of the possibility of achieving long-range FM with high T_C ($> \text{RT}$) in RE doped ZnO systems, since it is experimentally demonstrated that, with varying electron concentrations, high T_C can be obtained in n-type $\text{ZnO}:\text{Gd}$.³²

FIG. 4. The density of states of the pristine $\text{Zn}_{48}\text{O}_{48}$ nanowire without Gd dopants.

We also investigate the DOS, as it can provide further insight into the exchange mechanism. Fig. 4 depicts the DOS of pristine $\text{Zn}_{48}\text{O}_{48}$ nanowire, exhibiting a semiconducting and nonmagnetic nature, in line with previous calculations.³³ The upper part of the valence band (from -4 to 0 eV) is mainly due to O $2p$ states. However, the contribution of Zn d states becomes prominent in the -4 eV to -6 eV range, which is buried deeply inside the valence band. Zn $3d$ and O $2p$ states reveal an overlap between the electronic states, which results in strong hybridization. The Zn, O and Gd DOSs for the $\text{Zn}_{46}\text{O}_{48}\text{Gd}_2$ nanowire with and without V_O are shown in Fig. 5, in the top and bottom panels, respectively.

FIG. 5. The densities of states of the $\text{Zn}_{46}\text{O}_{48}\text{Gd}_2$ and $\text{Zn}_{46}\text{O}_{47}\text{Gd}_2$ nanowires (top and bottom panels), respectively. The projected density of states of Zn(s), O(p), Gd(d), and Gd(f).

The spin-up and spin-down DOSs of doped nanowire are significantly different from that of the pristine nanowire. For ZnO doped with Gd, a remarkable shift in the Fermi level into the conduction band, close to the Gd f states, is observed. The majority Gd f states (spin up) that are located well below the valence band maximum are fully occupied. On the other hand, the minority unoccupied Gd f states are localized in the vicinity of the Fermi level. The Gd d states in the conduction band overlap with the Gd f -states. Hybridization of the Gd f states with the states of the host material occurs at the Fermi level. As a result of introducing V_O , the Gd f state near the Fermi energy becomes partially occupied by donor electrons. Consequently, the carrier concentration around V_O is increased, which mediates interaction between the s (mostly from Zn) and f electrons. This is evident from the DOS, as the s - f coupling is more prominent than p - f and f - f couplings. Since d orbitals are not contributing to the partially filled energy bands, the double exchange picture is inappropriate for describing the exchange interaction in the current context of ZnO:Gd nanowires.³⁴ In this case, when Fermi level overlaps with the Gd f -state (which becomes partially filled) donor electrons occupy empty f states and thus FM coupling occurs.²³ The type of carriers involved in establishing long-range ferromagnetic order determines the exchange interactions in DMS materials. Zener's p - d exchange mechanism, as described by Dietl *et al.*¹ is weaker and long-ranged, mediated by extended band of the valence hole states. The double-exchange model is based on a physical picture of the d electron hopping between atoms with strong on-site exchange.³⁴ In the present study of ZnO:Gd nanowires, V_O donates two electrons to the system, mediating the ferromagnetic exchange and hence, the s - f coupling is more prominent than other mechanisms.^{34,35} According to our calculations, introducing V_{Zn} does not increase the ferromagnetic coupling energy. Moreover, p - f exchange interaction mediated by holes is not possible, as the calculated DOS of Gd-doped ZnO nanowire shows a shift of Fermi level towards the conduction band, implying that electrons can mediate FM through s - f interactions. Hence, it can be concluded that the increase in ΔE (up to 200 meV) with the introduction of V_O is due to this strong s - f coupling. Thus, the presence of V_O is crucial for increasing the s - f coupling (as $4f$ state is strongly localized) and therefore promotes long-range RTFM in Gd-doped ZnO nanowires.

IV. CONCLUSIONS

A systematic study of Gd doping in ZnO nanowires showed that the energetically favorable substitutional sites are located on the surface of the nanowire, which is in agreement with previous experimental observations. We have shown that the exchange coupling between the Gd atoms is sufficient for establishing RTFM. Introduction of additional charge or V_O increases the ferromagnetic coupling energy by enhancing the s - f coupling significantly, as Fermi level is shifted further into the conduction band, close to the Gd f states. Our findings can be used to understand experimentally observed RTFM in Gd-doped ZnO nanowires.

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