Investigated electronic structure and magnetic ordering of rare earth impurities (Eu, Gd) in ZnO

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First-principles calculations of the electronic structure of substitutional rare earth (RE) impurity (Eu and Gd) in wurtzite ZnO have been performed using density functional theory within a Hubbard potential correction to the RE 4f states. For Eu-doped ZnO, the magnetic coupling between Eu ions in the nearest neighbor sites is ferromagnetic (FM). The room temperature (RT) ferromagnetism (FM) can be enhanced by an appropriate hole doping into the sample. The ZnO:Gd is found to favor the antiferromagnetic (AFM) phase. The FM can be achieved by high electron doping. The native defects effect (VO, VZn) on the FM is also studied. The oxygen vacancies seem to play an important role in the generation of the FM in both ZnO:Eu and ZnO:Gd, which is in good agreement with recent experimental results.

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1. Introduction

Rare earth (RE)-doped semiconductors show high interest for spin electronics, since the observation of ferromagnetism (FM) in Gd-doped GaN, with Curie temperature larger than 400 K1-3 and a colossal magnetic moment of 400 𝜇b/Gd. Experimental
results strongly suggest that defects play an important role in the FM in GaN:Gd, but there has been no identification of these defects. From first-principles studies, the origin of the colossal magnetic moment is due to the coupled orbital states as well as defect induced FM.

For ZnO, experimental reports are available on FM in Gd-doped ZnO with conflicting results. Ferromagnetic (FM) like behaviour was found at room temperature (RT) samples prepared by pulsed spray pyrolysis and also for ion-implanted samples which was enhanced by annealing. Pulsed-laser deposited samples with low Gd content were reported to be paramagnetic, and they turn FM below 150 K for an increased Gd content of 1%. Ney et al. have elaborated paramagnetism in Zn$_{1-x}$Gd$_x$O epitaxial films prepared by reactive magnetron sputtering with nominal Gd concentrations of up to 16%, and corroborated their results by first-principles calculations. RT FM has also been reported in Zn$_{1-x}$Eu$_x$O polycrystalline films and nanocrystals, but understanding its mechanism remains a controversial issue.

Moreover, first-principles studies have also produced contradictory conclusions. Shi et al. using the pseudopotential method within generalized gradient approximation (GGA), have detailed that for cubic Gd-doped ZnO, the magnetic coupling between Gd ions in the nearest neighbor sites is FM and that its stability may be enhanced by appropriate electron doping. Bantounas et al. have suggested that the introduction of the Hubbard $U$ parameter to the Gd $f$ states favors an antiferromagnetic (AFM) phase in wurtzite Gd-doped ZnO. Caroena et al. using the full-potential linearized augmented plane wave (FP-LAPW) method within the GGA + $U$, have investigated the electronic properties of lanthanide (from Eu to Tm) impurities in wurtzite GaN and ZnO. They have reported that the RE impurities stay in a 3+ oxidation state in both materials, and that the RE-doped ZnO became an $n$-type material showing a coupling between the 4$f$-related spin polarized states and the carriers which may generate spin polarized currents. Hachimi et al. using the FP-LAPW method within the GGA, have investigated the electronic structure and magnetic properties of the RE-doped ZnO (RE = La–Yb). They have shown that the substitution of RE ions in ZnO induced spins polarized localized states in the band gap, and that RT FM was possible when the two RE impurities were nearest neighbors. Zhang et al. using the projector-augmented wave method within the GGA + $U$, have studied the electronic structure and magnetism of RE-doped ZnO (RE from La to Eu). For Eu-doped ZnO, they have reported that the magnetic ground states of Eu-doped ZnO system display weak AFM.

In this work, the electronic structure of Eu and Gd impurities in wurtzite structure is elaborated by performing total energy and band structure calculations. The strong correlation of the RE $f$-electrons was taken into account using the local spin-density approximation (LSDA) with the additional Hubbard correlation term. By considering both the FM and AFM couplings between the two RE atoms at Zn sites in a $(2 \times 2 \times 2)$ supercell, we found that Eu dopants preferentially present FM
coupling while the ground state of Gd dopants is AFM. The properties of FM coupling between RE ions in different charged states to determine if the electrons and holes with different concentrations can mediate the FM in the ZnO:RE systems are also studied. We have also investigated whether the intrinsic defects V\textsubscript{Zn}, V\textsubscript{O} play an important role in the generation of the FM in ZnO:RE systems. It is the first quantitative theoretical prediction of the origin of the FM in ZnO:Gd and ZnO:Eu using Hubbard corrections.

The present paper is organized as follows: Section 2 presents the details of the calculations. The results and discussions are elaborated in Sec. 3, and Sec. 4 presents the conclusions.

2. Calculations Details

The electronic structure calculations are based on the density-functional theory in the LSDA with the additional Hubbard correlation term which describes on-site electron–electron repulsion associated with the 4\textit{f} narrow bands (LSDA + \textit{U} approach)\textsuperscript{19,20}. The first-principles band-structure approach applied in this work is the scalar relativistic full-potential linear-augmented-plane-wave plus local orbital (FP-LAPW + lo) method\textsuperscript{21,22} (Wien2k implementation\textsuperscript{23}).

The wurtzite RE-doped ZnO was modeled using supercell of 32 atoms. In the calculations, we substitute two Zn atoms with two RE ions in the nearest neighbor sites, which corresponds to a RE concentration of 12.5%. The atomic structure is shown in Fig. 1. The Zn 3\textit{d} and RE 5\textit{p} 4\textit{f} electrons are explicitly treated as valence electrons. We have used muffin-tin radii of 2.1 Bohr for both RE and Zn and 1.5 Bohr for O. In the total-energy calculation, the factor $R_{\text{mt}} k_{\text{max}}$ is chosen to be 7 and all the geometries are optimized until the quantum mechanical forces acting

![Fig. 1. Illustration of the 2 x 2 x 2 supercell of the REZnO.](1650225-3)
on the atoms are smaller than 0.01 eV/Å. The Brillouin-zone integrations were performed using $3 \times 3 \times 2$ Mokhorst–Pack special $k$-points.\textsuperscript{24}

3. Results and Discussion

In order to model the highly correlated $4f$-related electronic states, we used on-site Hubbard potential correction computed self-consistently by Madsen and Novak method,\textsuperscript{25,26} for the $4f$ states of the RE atoms. This method describes the electronic correlation of the transitions metals $d$ states\textsuperscript{25} and RE $f$ states\textsuperscript{16} appropriately. The structural properties as well as the obtained Hubbard $U_{4f}$ values are given in Table 1. The results show that the calculated lattice constant for ZnO is slightly underestimated in comparison to the experimental value,\textsuperscript{27} which is well known of local density approximation (LDA). The structure of ZnO:Eu and ZnO:Gd expands in comparison with pure ZnO crystal, which is natural because Eu and Gd with larger ionic radius replaced Zn with smaller ionic radius.

According to the optimized lattice structure, we calculate the energy band structure as shown in Fig. 2 for ZnO and for FM ZnO:Eu and ZnO:Gd. The spin-direction

\begin{table}[h]
\centering
\begin{tabular}{lll}
\hline
 & $a$ (Å) & $c$ (Å) & $U$–$J$ (eV) \\
\hline
ZnO & 3.2101 & 5.1843 & LSDA \\
 & 3.2489 & 5.2066 & \\
Eu$_{0.125}$Zn$_{0.875}$O & 3.3214 & 5.3604 & \textsuperscript{a}8.19 \\
Gd$_{0.125}$Zn$_{0.875}$O & 3.3156 & 5.3506 & \textsuperscript{b}7.21 \\
\hline
\end{tabular}
\caption{The optimized lattice constants $a$ and $c$ of pure ZnO, Eu$_{0.125}$Zn$_{0.875}$O and Gd$_{0.125}$Zn$_{0.875}$O within the values of the Hubbard parameter used for Eu and Gd atoms (Experiment results for ZnO are from Ref. 28\textsuperscript{a}).}
\end{table}

Fig. 2. The calculated electronic band structure of (a) pure ZnO, (b) Eu$_{0.125}$Zn$_{0.875}$O and (c) Gd$_{0.125}$Zn$_{0.875}$O.
Investigated electronic structure and magnetic ordering of RE impurities

![Graph showing total and partial DOS of Zn, O and RE atoms](image)

**Fig. 3.** Total and partial DOS of Zn, O and RE atoms in (a) Eu$_{0.125}$Zn$_{0.875}$O and (b) Gd$_{0.125}$Zn$_{0.875}$O.

is taken as the direction of the RE spin ($\uparrow$ for majority spin direction and $\downarrow$ for minority one). All energies are relative to the respective Fermi level. Compared with the band structure of pure-ZnO, we note that the Fermi energy is going into the conduction band after doping RE. This is due to the fact that valence band shifting into the lower energy region is much more than that of the conduction band. The band gap of ZnO:RE (RE = Eu and Gd) decreases from 0.79 eV of pure ZnO to 0.67 eV and 0.65 eV for ZnO:Eu and ZnO:Gd, respectively. Figure 3 displays the total and partial densities of state (DOS) of ZnO:RE. The 4$f$ orbitals split into three parts due to the tetrahedral field: the lowest energy triply degenerate $t_{1g}$, triply degenerate $t_{2g}$ and singly degenerate with the highest energy state $a_{2g}$. We can see that the valence band is divided into two regions. The lower valence band within $\sim -22.8$ to $-17.5$ eV for ZnO:Eu and from $\sim -24.6$ to $-18.4$ for ZnO:Gd is mainly contributed by the O 2$s$ and RE 5$p$ states. The upper valence band of ZnO:Eu exhibits a hybridization from $\sim -9.8$ to $-6.2$ eV between Zn 3$d$ and O 2$p$ states, and hybridization from $-7.2$ to $-2.7$ eV between occupied Eu 4$f$ ($t_{1g}$ and $t_{2g}$) and O 2$p$ states. The $a_{2g}$ 4$f$ states of majority spin are located near the Fermi level and partially occupied while those of minority spin are unoccupied and located 4.8 eV above $E_F$. For ZnO:Gd, from $\sim -9$ to $-7$ eV the hybridization is between Gd 4$f$, Zn 3$d$ and O 2$p$ states. The bands located from $-7$ to $-2.8$ eV derive from the O 2$p$ states with a small contribution of Zn 3$d$ states. The unoccupied Gd 4$f$ states are located 3 eV above the Fermi level.
In our calculations, we took the isoelectronic trivalent configuration of the RE since in experimental studies\textsuperscript{12,13} FM behavior at RT has been shown in samples where Eu is in the +3 oxidation state. From the theoretical side, Caroena et al.\textsuperscript{16} using the FP-LAPW method and GGA + $U$, have reported that all RE impurities in ZnO (RE from Eu to Tm) stay in 3+ oxidation state in which RE donates two electrons to stabilize the binding with the oxygen neighboring atoms, while the third electron populates the bottom of the ZnO conduction band. In our calculations, the $a_2g\ 4f$ states of majority spin of ZnO:Eu (Fig. 3) interact with delocalized energy level that defines the conduction band bottom. As the latter is occupied by almost-free carriers, this indicates the possibility of getting spin polarized carriers. This is not the case of the ZnO:Gd, where the $4f$ states are located 3 eV above the Fermi level. Our results are in good agreement with those of Caroena et al.\textsuperscript{16} for ZnO:Gd and ZnO:Eu and in disagreement with those of Shi et al.\textsuperscript{14} for ZnO:Gd. This later uses the pseudopotential method within GGA, has reported that the $4f$ bands of majority spin are found far from the Fermi energy, lying at about $-20$ eV. Since GGA does not give a significant change on band structure, in comparison to the LDA, we calculated the band structure of ZnO:Gd using the LSDA; the majority spin $4f$ bands are located at the valence band maximum (VBM). Hachimi et al.\textsuperscript{17} have given the same result for Gd-doped ZnO, who have used the FP-LAPW within the GGA. For Eu-doped ZnO, Zhang et al.\textsuperscript{18} using the GGA + $U$, have reported that the $4f$ states are located between the valence and conduction bands. This is probably due to the differently used Hubbard $U$ parameter and the application of the Hubbard corrections to the Zn 3$d$ states.

The total magnetic moment per supercell is 12.41 $\mu_B$ for ZnO:Eu, 13.98 $\mu_B$ for ZnO:Gd and the localized RE magnetic moment is 6.06 and 6.90 $\mu_B$, for Eu and Gd, respectively. The O atoms being the nearest neighbors of RE atoms possess the largest RE induced magnetic moment with a negative contribution of $-0.03$ and $-0.02$ $\mu_B$, for ZnO:Eu and ZnO:Gd, respectively. The Zn atoms contribute fairly to the total magnetic moment with small positive moment (MM $\sim 10^{-4} \mu_B$). The second neighbors have a magnetic moment of $\sim 10^{-3} \mu_B$ for ZnO:Eu and $\sim 10^{-4} \mu_B$ for ZnO:Gd for O atoms and $\sim 10^{-5} \mu_B$ for Zn atoms for both systems, which make the evidence of the highly localized influence of RE ions.

For ZnO:Eu and ZnO:Gd, RT FM has been reported\textsuperscript{6–9,11–13} but understanding its mechanism still remains a controversial issue. For ZnO:Eu, it was reported that the FM was due to the intrinsic properties of Eu-doped ZnO films and could be interpreted by the bound magnetic polaron (BMP) model. Also, Eu-doped ZnO nanocrystals\textsuperscript{12} have shown FM behavior at RT in which the magnetic response increases as Eu$^{3+}$ ions concentration increases. Since Eu$^{3+}$ is not a magnetic ion, the intrinsic exchange interaction of magnetic moment mediated by defects in Eu-doped ZnO nanoparticulate powder may be ruled out.\textsuperscript{13} The intrinsic defects in ZnO are suspected to be the origin of the FM.\textsuperscript{13} It was reported\textsuperscript{13} that in samples of $x = 0.03$ where the Eu$_2$O$_3$ phase was detected, the latter may enhance the intrinsic defects in ZnO lattice such as zinc and oxygen vacancy, thus the magnetism. Further, the
Table 2. Calculated energy differences $\Delta E$ ($\Delta E = E_{\text{AFM}} - E_{\text{FM}}$) between AFM and FM configurations for ZnO:Eu and ZnO:Gd in different charged states.

<table>
<thead>
<tr>
<th>Charge state</th>
<th>Eu</th>
<th>Gd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>7.11</td>
<td>-0.92</td>
</tr>
<tr>
<td>0.15e/RE</td>
<td>-7.14</td>
<td>-1.54</td>
</tr>
<tr>
<td>0.25e/RE</td>
<td>-11.34</td>
<td>-1.53</td>
</tr>
<tr>
<td>0.50e/RE</td>
<td>-32.58</td>
<td>-1.07</td>
</tr>
<tr>
<td>0.75e/RE</td>
<td>-39.41</td>
<td>0.24</td>
</tr>
<tr>
<td>1.00e/RE</td>
<td>-2.18</td>
<td>7.1</td>
</tr>
<tr>
<td>0.50h/RE</td>
<td>15.37</td>
<td>-0.28</td>
</tr>
<tr>
<td>1.00h/RE</td>
<td>0.63</td>
<td>0.21</td>
</tr>
<tr>
<td>V_{Zn}</td>
<td>1.05</td>
<td>0.14</td>
</tr>
<tr>
<td>V_{O}</td>
<td>14.92</td>
<td>1.23</td>
</tr>
</tbody>
</table>

oxygen vacancies present in the samples due to the stabilization of the structure increase with the Eu$^{3+}$ doping concentration.\textsuperscript{12} For ZnO:Gd, the defect-like oxygen vacancies are suspected also to be the origin of the observed FM behavior in the samples.\textsuperscript{28}

In order to analyze how defects mediate the FM in ZnO:Eu and ZnO:Gd systems, the properties of FM coupling between RE ions in different charged states are investigated. To this end, we simulated the effect of donors (acceptors) by introducing electrons (holes) into the ZnO:RE systems and also determined whether intrinsic defects ($V_{\text{Zn}}$, $V_{\text{O}}$) play a significant role on the magnetic properties. The $V_{\text{Zn}}$ and $V_{\text{O}}$ are chosen to be the nearest neighbors to RE ions. Our calculated results are listed in Table 2. The obtained direct coupling between 4$f$ electrons in ZnO:Gd and ZnO:Eu is very weak compared to the energy difference $\Delta E$ of 3$d$ TMs doped ZnO.\textsuperscript{29,30} This is because the orbitals of 4$f$ electrons have a highly localized character.

To understand the doping dependence of $\Delta E$, we have also calculated the partial and total DOS of ZnO:Eu and ZnO:Gd in the FM and AFM state for one electron and one hole doping drawn within those of the neutral case. The DOS of ZnO:Eu are shown in Fig. 4 and those of ZnO:Gd in Fig. 5. For both ZnO:Eu and ZnO:Gd, the DOS of AFM state (Figs. 4 and 5) show a similar feature as the FM state except for the RE-$f$ states, i.e., in the AFM situation the magnetic moments of two RE atoms in the supercell have opposite direction for each other so that total DOS are symmetric in the spin direction.

Our results show that the position of 4$f$ states and their hybridization effect with the VBM $p$-bands, as well as with the conduction band minimum (CBM) $s$-bands ($s$–$f$ interaction), can be substantial if the $f$ bands are close in energy to the gap edges. For ZnO:Eu, the ground state is FM in neutral state, and the energy difference $\Delta E = E_{\text{AFM}} - E_{\text{FM}}$ is 7.11 meV. In the FM phase, the exchange splitting $\Delta E_c$ is 0.07 eV at the CBM while the splitting $\Delta E_v$ at the VBM is 0 eV (Fig. 2).
Fig. 4. Total and 4f RE partial DOS of FM and AFM EuZnO in the neutral case, 1 electron and 1 hole doping.

Therefore, the FM coupling between two Eu atoms is dominated by electrons due to the exchange splitting of the conduction band from the coupling between f electrons and host s electrons. When electrons are inserted, the ZnO:Eu favors the AFM phase and $\Delta E$ varies from $-7.14$ meV for 0.15 electron to $-39.41$ meV for 0.75 electron (Table 2). For 0.15, 0.25, 0.5 and 0.75 electrons, the $\Delta E_v$ remains 0 and $\Delta E_c = 0.077$ eV. The DOS show that the doped electrons were supplied mainly to spin up Eu $a_{2g}$ 4f states (Fig. 4), but it is not sufficient to valorize the double exchange, and the system energy is lowered by AFM spin alignment of
Investigated electronic structure and magnetic ordering of RE impurities

Fig. 5. Total and 4f RE partial DOS of FM and AFM GdZnO in the neutral case, 1 electron and 1 hole doping.

the neighboring Eu atoms by super exchange. When 1 electron is added, which is sufficient to the double exchange, the material shows a decreasing spin-splitting at the CBM of 0.05 eV and a strong negative spin splitting of the valence band of $-0.54$ eV (Fig. 4) which means that the exchange interaction at the VBM is AFM. This explains the fact that the ZnO:Eu stays in the AFM state with a decreasing of the value of $\Delta E$ to $-2.18$ eV. For oxygen vacancies, which added 2 electrons, the ZnO:Eu stabilizes in the FM phase with $\Delta E$ of 14.92 meV. For hole doped cases, the ZnO:Eu favors the FM phase. As shown in Fig. 4, it results in completely empty
conduction bands ($E_f$ moves to the VBM), which favors the FM mediated by double exchange, where if the $f$ orbital is partially occupied then the electrons in that orbital are allowed to hop to the neighboring $f$-orbitals, provided the neighboring Eu atoms are in the parallel spin configuration. Thus, the $f$-electrons lower the kinetic energy by hopping in the FM state. For Zinc vacancies, which contribute with two holes to the system, our calculated $\Delta E$ is 1.05 meV, i.e., the ZnO:Eu system prefers FM phase. So, the ZnO:Eu prefers the FM phase in the ground state and the FM is enhanced if oxygen vacancies and intermediate doping of hole are achieved. Our results confirm the experiment observation, which report FM and an increasing magnetic response within the Eu$^{3+}$ concentration and oxygen vacancies.

For the ZnO:Gd, the ground state is AFM and the energy difference between AFM and FM coupling states $\Delta E = E_{AFM} - E_{FM}$ is $-0.92$ meV (Table 2). In the FM case (Fig. 2), the spin-splitting at the band edge is weak ($\Delta E_{c} = 9$ meV and $\Delta E_{v} = 0$), therefore, it will not lead to any energy gain compared to the unsplit band edge of the AFM phase. The substitution of Zn with Gd does not bring any carriers in the system, and if no carrier is introduced additionally, the AFM ordering is more stable than the FM one. When electrons are inserted, the system still favors the AFM phase for the concentration of 0.15, 0.25 and 0.5 electrons (Table 2). For the latter, and as for the neutral case, the spin splitting at VBM and CBM is negligible. When 0.75 or 1.0 electron is injected into the system, the ZnO:Gd favors the FM phase with $\Delta E = 0.24$ and 7.1 meV, respectively. It was found by analyzing the calculated DOS (Fig. 5), that they do not occupy the $4f$-Gd states. The electrons were supplied mainly to the host conduction band. As a result, an energy gains by the double exchange interaction between the two Gd ions through O atom is not expected and the FM state is not stabilized for the case of 0.25 and 0.5 electron. As the concentration of electron increases, the $f$ states move slightly downward. When 0.75 and 1 e were inserted, the $f$ states are moved up to 1 eV downward (Fig. 5), which increase the $s–f$ coupling resulting on a negative and weak spin-exchange splitting of CBM ($-5$ meV). Consequently, when 1 electron is added, it prefers to go to the spin down CBM of the FM phase, stabilizing the FM configuration. When holes are inserted, the AFM state becomes unstable (for 0.5 hole) and the FM state becomes the ground state (for 1 hole). The DOS show that $E_f$ is moved downward at the VBM, which results in completely empty conduction bands. The holes enhance the carrier concentration, which leads to an energy gain and stabilizes the FM states. For Zinc vacancies, which contributes two holes to the system, our calculated $\Delta E$ is 0.14 meV, i.e., the ZnO:Gd system favors FM phase. The $V_O$ leads the system to FM phase with $\Delta E = 1.23$ meV. So, the ZnO:Gd favors the AFM phase in the ground state and presents a FM if oxygen vacancies and a high doping of electrons such as 0.75 and 1.0 electron per Gd are achieved.

In our study, the electronic and magnetic properties of europium and gadolinium substituting in wurtzite ZnO by taking into account the strong correlation of the RE $f$-electrons using the LSDA + $U$ approach are investigated. The LDA + $U$
(GGA + $U$) method has been used with considerable success in the description of electronic structure and magnetism\textsuperscript{31–34} of the highly correlated systems. It is shown that the self-consistent procedure to compute the values of the Hubbard $U$ parameters provides a reliable description of the electronic properties of those REs. By accurate description of the $f$ states, and by considering both the FM and AFM couplings between the two RE atoms at Zn sites, we have investigated the electronic structure and the ground state of ZnO:RE in the neutral state and study their electronic and magnetic properties in different charged state to get an answer on the role played by defects on mediating the FM in the ZnO:Eu and ZnO:Gd systems. For intrinsic defects ($V_{Zn}$, $V_O$), and to get a definitive conclusion on their role, it will be necessary to study the effect of their position and the variation of their concentration on electronic and magnetic properties.

4. Conclusion

Electronic structure and magnetic ordering of ZnO:Eu and ZnO:Gd have been investigated by taking into account the strong correlation of the RE $f$-electrons using the LSDA + $U$ approach. Doping ZnO with Eu leads to $n$-type doping, since the $4f$ states are found to interact with delocalized energy level that defines the conduction band bottom, which is not the case of the ZnO:Gd. This result indicates the possibility of getting spin polarized carriers in ZnO:Eu. We also investigated the magnetic properties of the ZnO:RE in different charged states and within native defects ($V_{Zn}$, $V_O$). For ZnO:Eu, the ground state is FM coupling state. The FM can be enhanced by an appropriate hole doping and the injection of oxygen vacancies. For ZnO:Gd, our results show an AFM phase in the ground state and present a FM if oxygen vacancies and high doping of electrons are achieved. The injection of zinc vacancies generates a weak FM in comparison to those of oxygen ones. However, to get a conclusion on the role of the native defects ($V_{Zn}$, $V_O$), it is imperative to study the effect of their position and the variation of their concentration on magnetism, which will be pursued in our future research.

Research Highlights

Electronic structure of Gd and Eu substituting in wurtzite ZnO has been investigated using the LSDA + $U$. The FM coupling between RE ions in different charged states are studied. For ZnO:Eu the FM can be enhanced by an appropriate hole doping and the injection of oxygen vacancies. The ZnO:Gd present a FM if oxygen vacancies and high doping of electrons are achieved.

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