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Defect induced d^0 ferromagnetism in a ZnO grain boundary

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Several experimental studies have referred to the grain boundary (GB) defect as the origin of ferromagnetism in zinc oxide (ZnO). However, the mechanism of this hypothesis has never been confirmed. Present study investigates the atomic structure and the effect of point defects in a ZnO GB using the generalized gradient approximation+ U approximation. The relaxed GB possesses large periodicity and channels with 8 and 10 numbered atoms having 4 and 3 fold coordination. The Zn vacancy (V_{Zn}) shows a tendency to be attracted to the GB, relative to the bulk-like region. Although no magnetization is obtained from point defect-free GB, V_{Zn} induces spin polarization as large as $0.68 \mu_B/\text{atom}$ to the O sites at the GB. Ferromagnetic exchange energy >150 eV is obtained by increasing the concentration of V_{Zn} and by the injection of holes into the system. Electronic structure analysis indicates that the spin polarization without external dopants originates from the O $2p$ orbitals, a common feature of d^0 semiconductors. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4936659>]

I. INTRODUCTION

Recent years have witnessed enormous interest in zinc oxide (ZnO), due to its potential optoelectronic and spintronic applications, such as in light emitting diodes and spin-polarized solar cells, as ZnO offers the possibility of combining semiconducting and magnetic effects.^{1–4} The realization of these technologies depends on the development of room temperature ferromagnetism (RTFM) in ZnO. Even though doping ZnO with transition metals (TMs) is a widely employed technique,⁵ many studies failed to reproduce the long-range RTFM.^{6,7} In some extant studies, the observed FM has been attributed to the secondary phases and clusters formed in ZnO.⁸ Irrespective of all these controversies, it has been widely accepted that a subtle balance between many types of defects plays a key role in the RTFM of ZnO. Several authors have reported spin polarization in ZnO induced by cation vacancies,^{9,10} which arises from localized holes forming triplet states at a stable magnetic ground state. Since these localized holes are located in the p -band, rather than in the d -band, this phenomenon is referred to as d^0 FM.^{11–14} It has been proven to be an alternative to TM doping, as the magnetization originates in the presence of sufficient holes. However, the formation energy (E^f) of cation vacancy in bulk ZnO is high, making the achievement of FM difficult. One of the methods suggested to reduce the E^f of cation vacancies in bulk ZnO is a co-doping approach.¹⁴ In another study, Singh *et al.*¹³ have found that cation vacancies can be easily formed in ZnO nanoclusters whereby d^0 magnetism originate from O $2p$ orbitals due to the dangling bonds created by these cation vacancies. Nevertheless, intrinsic point defects can be easily formed in ZnO samples, along with other structural

defects (dislocations, stacking faults, and grain boundaries (GBs)) and presence of these structural defects is found to be crucial in modifying the electrical, magnetic, and optical properties of ZnO.^{2,15,16} Particularly, the coordination number of atoms in a GB is different from that in the bulk and over- or under-coordination of atoms can exist at the GBs, which in turn will modulate the properties of polycrystalline materials. The presence of dangling or distorted bonds at the GB can facilitate native defect formations and dopant segregations. The role of GB in promoting RTFM in ZnO is suggested in the experimental studies.^{2,3,17} Magnetic force microscopy has predicted that intrinsic and extrinsic defects at GBs can be the origin of the FM observed in Mn doped ZnO thin films.¹⁷ However, the contribution of GBs in ZnO in promoting RTFM is not studied in detail and can be understood only through a systematic and microscopic study that incorporates varied concentrations of point defects at the GBs.

The properties of polycrystalline materials are intimately related to the atomic structure of GBs; hence, the effect of different GBs on the material properties will be different. Simulations on well-defined GBs are thus essential as it is possible to have wide variety of GB atomic structures, depending on the orientation relationships of the GB planes and the translation states of the two adjacent grains influencing the material behavior.^{18,19} Experimentally, it is possible to obtain GBs with low (approximately $<15^\circ$)¹⁸ and high angles^{19,20} that possess different characteristics. Therefore, the atomic structure of each GB will be unique and the GB properties can be improved by tuning the atomic structure. Existing studies on various ZnO GBs mostly investigate the electrical properties focusing on the various applications of ZnO.²¹ In this scenario, magnetism in polycrystalline ZnO containing point defects at the GB presents an interesting research problem from the fundamental and technological point of view. This motivated us to investigate the contribution

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of a GB containing point defects towards the origin of RTFM in ZnO. Zn and O vacancies (henceforth referred to as V_{Zn} and V_{O} , respectively) are introduced at the GB to understand the contribution of GB-defect complexes to the RTFM of undoped ZnO.

II. COMPUTATIONAL METHODOLOGY

The GB is formed by attaching two wurtzite (0001) ZnO crystals oriented at an angle of 45° relative to each other, individually having 148 atoms, and the supercell contains 296 atoms. The calculations are performed using the pseudopotential method based on density functional theory as implemented in the Vienna *ab initio* simulation package within the generalized gradient approximation (GGA).^{22,23} The pseudopotentials are based on the projector augmented wave formalism.²⁴ The atomic coordinates are relaxed with energy and force tolerances of 0.001 eV and 0.001 eV/Å, respectively, and relaxation is conducted on both neutral and charged supercells. Cut-off energy of 400 eV is used to expand the plane waves included in the basis set and Brillouin zone sampling is carried out in the Monkhorst-Pack scheme using a $1 \times 1 \times 6$ k-point mesh. Owing to the strong electronic correlations of the $3d$ electrons, standard density functional theory fails to accurately describe the electronic structure of ZnO. Therefore, the GGA+ U method with on-site Coulomb parameter $U = 7$ eV with a J value of 1 eV ($U - J = 6$) is used in the Duradev's approach.²⁵ The choice of U and J is validated by comparing the calculated values of the lattice parameter with experimental values. The calculated bulk unit cell parameters are $a_0 = b_0 = 3.32$ Å and $c_0 = 5.219$ Å, which is in good agreement with the experimental findings ($a_0 = b_0 = 3.2507$ Å; $c_0 = 5.2083$ Å).²⁶ These optimized values of bulk lattice parameters are used for constructing the GB supercell, such that $a = 7 \times a_0$, $b = \sqrt{3} \times 3 \times b_0$, and $c = c_0$. Such a large supercell ensures negligible interaction between the periodically repeated GB images. The formation energy (E^f) of native defects, such as V_{Zn} and V_{O} , is calculated

using the expression²⁷

$$E^f(D) = (E_{\text{tot}}(D) - E_{\text{tot}}(\text{ZnO}) + n_i \mu_i + q E_F) / n_i, \quad (1)$$

where $E_{\text{tot}}(D)$ is the total energy of the ZnO supercell containing the defective GB, and $E_{\text{tot}}(\text{ZnO})$ is the total energy of same supercell without point defects at the GB. Here, n_i and μ_i are, respectively, the number and chemical potential (which is dependent on the experimental growth conditions) of the atoms removed from the supercell. Extreme O-rich conditions are represented by the energy of O in the O_2 molecule, while that of Zn is given by the energy of bulk Zn. Finally, q denotes the charge state and E_F is Fermi energy. The inclusion of E_F accounts for the various charge states in which defects can occur.

III. RESULTS AND DISCUSSION

A. Structure and energetics

The atomic coordinates of the GB are allowed to relax without any constraints and the geometry before and after relaxation is shown in Fig. 1. It can be seen from Fig. 1 that the two ZnO single crystals are directly bonded at the GB and no inter-granular structures are formed at the boundary. Structural units in which the Zn and O atoms are 4 and 3 fold coordinated appear at the GB after relaxation, in contrast to the bulk ZnO having 4 fold coordination. The relaxed GB is stable with no Zn–Zn or O–O “wrong bonds” and consists of channels with 8 and 10 membered atoms, compared to the 6 atom open channel in bulk ZnO. The 8 and 10 atom ring patterns are repeated, indicating that the atomic arrangement is periodic at the GB. A closer look at the bond lengths at the GB indicates that, after optimization, the Zn–O bonds undergo slight change of ~ 0.05 Å in the 8 and 10 membered rings compared to the bulk, to minimize the local forces in the vicinity of the GB.

To investigate the effect of the presence of intrinsic point defects at the GB on the structural, electronic, and magnetic properties, we introduce single V_{Zn} and V_{O} at the GB, with

FIG. 1. ZnO GB structure before (a) and after (b) relaxation. The grey and pink atoms indicate Zn and O, respectively.

FIG. 2. Relaxed GB; the examined Zn vacancy positions are indicated with V_i symbols ($V_1, \dots, V_{14}$) along with their E^f (in eV). The grey and pink atoms indicate Zn and O, respectively. Note that the most favorable vacancy position is V_7 at the GB.

atomic relaxation carried out for each case. This amounts to a vacancy concentration of 0.34% in the ZnO supercell. The E^f of these defects is calculated according to Equation (1). While carrying out the calculations for E^f , we have not included any image charge corrections. For calculations involving semiconductors with smaller supercells, the electrostatic and elastic interactions between the defects and their periodic images can be significant and converge rather slowly with the size of the supercell. On the other hand, the effects of these interactions were found to be negligible in the dilute limit for larger supercell sizes.⁴ Since we are not concerned with investigations on the formation energies of isolated defects and have considered a comparatively larger supercell with 296 atoms, our results will not alter significantly if the image charge corrections were taken into account. Although it is known that neutral V_O is more stable than V_{Zn} in bulk ZnO,²⁷

E^f shows that the opposite is true at the GB. Since the 45° GB has relatively long structural periodicity along the GB plane, a systematic investigation on the preference of atomic site of vacancies is inevitable. Motivated by the low E^f and favorable magnetism exhibited by V_{Zn} , we have analyzed 14 Zn vacancy sites at the GB as shown in Fig. 2. It can be seen that the most favorable V_{Zn} position is located at a neck site in the 8 atom membered ring (V_7) with 3-fold coordination (the E^f values for all V_{Zn} positions (V_1 to V_{14}) are indicated in Fig. 2).

The Zn–O bond length contraction near V_7 is ~ 0.1 Å, in average, to adjust the local strain in the vicinity of the GB. We find that V_{11} (3.8 eV) and V_{15} (4.07 eV) also possess very low E^f with 3-fold coordination at the GB. Hence, it is easier to break these bonds relative to those formed at 4 fold-coordinated sites in the GB. For V_O , five different positions are considered and their respective E^f values are given in Fig. 3.

FIG. 3. Relaxed GB; the examined O vacancy positions are indicated with symbols V_1 – V_5 . The E^f (in eV) is also shown. The grey and pink atoms indicate Zn and O, respectively. Note that the most favorable vacancy position is V_2 at the GB.

For comparison, E^f is also calculated for V_{Zn} and V_O located in the bulk-like region away from the GB. Interestingly, V_O also forms more easily in the GB ($E^f = 4.1$ eV; see Fig. 3), compared to bulk-like region ($E^f = 5.3$ eV). However, V_{Zn} is more stable at the GB with $E^f = 3.69$ eV (see Fig. 2) relative to the bulk-like region ($E^f = 5.10$ eV). We find that E^f of V_{Zn} at the GB is lower than in bulk ZnO ($E^f = 5.4$ eV).^{28,29} This finding indicates that the GB can stabilize V_{Zn} . Creating V_{Zn} by equilibrium or non-equilibrium processes yields p -type conductivity in ZnO. Therefore, this is in accordance with the previous observations where p -type conductivity in ZnO has been attributed to the impurities and vacancies at the GBs.³⁰ Even though the E^f of these intrinsic vacancies is high, they are unavoidable during growth, depending on the growth conditions and thermal fluctuations that occur during the process. Our study indicates that engineering GBs in polycrystalline samples assists in stabilizing V_{Zn} in ZnO, in agreement with the previous reports,³¹ whereas in bulk ZnO, V_O is more stable. However, the stability of vacancies depends to a great extent on the experimental growth conditions. In electron paramagnetic resonance (EPR)³² and positron annihilation spectroscopy (PAS)³³ experiments, V_{Zn} has been detected in ZnO samples. Hence, during non-equilibrium growth processes, anion vacancies in ZnO are less stable compared to cation vacancies, although they are found to be more stable at RT.^{32,34,35}

The E^f of defects might also depend on E_F —the electronic chemical potential. Hence, we have calculated the E^f as a function of E_F , for both Zn-rich (O-poor, ideal for O vacancy) and O-rich (Zn-poor, ideal for Zn vacancy) conditions and the corresponding results are presented in Fig. 4. Here, V_{Zn} is expected to act as a singly or doubly ionized acceptor; therefore, E^f is calculated for the neutral, -1 and -2 charge states. Since V_O is a donor defect 0 , $+1$, and $+2$ states are considered. The valence band maximum (VBM) is taken as the zero of the Fermi level and E_F is varied for each charge state as shown in Figs. 4(a) and 4(b) for O-rich

and Zn-rich conditions, respectively. For each charge state, the favorable value of E^f is shown, whereby the kink in the graph indicates the charge transition. Fig. 4(a) shows that for O-rich conditions, -2 charge state is most favorable for V_{Zn} (V_{Zn}^{-2}), with the increase in E_F , for n -type conductivity. However, for p -type conductivity, neutral V_{Zn} is the most stable compared to charged cation defects, whereas doubly charged V_O (V_O^{+2}) is more stable than neutral V_{Zn} , indicating V_O^{+2} is more favorable than V_{Zn} in the case of p -type conducting regime. Furthermore, neutral V_O and singly charged V_O^{+1} states are not favored for the O-rich conditions. In Zn-rich conditions, (Fig. 4(b)), E^f of both neutral and negatively charged V_{Zn} is high and decreases for V_{Zn}^{-2} with the increase in the Fermi level in the n -conducting regime. For V_O , the $+2$ charge state is more favorable for p -type conductivity and E^f increases with the increase in E_F . Conversely, neutral state of V_O shows high E^f compared to V_{Zn}^{-2} . Fig. 4 shows that V_O can only be formed at a low concentration in equilibrium Zn-rich and O-rich conditions as its E^f is high in both cases, which is in line with bulk ZnO.²⁷ However, in p -type conducting regime, V_O can be an active compensation center in ZnO due to its low E^f , as has been observed in other studies.²¹

Further, a pair of V_{Zn} is introduced at the GB to study the effect of vacancy concentration on the structural and magnetic properties, such that the vacancy concentration now amounts to 0.68% in the ZnO supercell. Different pair configurations are considered to examine the vacancy stability and magnetic coupling. To create a pair, we combine V_7 (the most stable site) with a second vacancy (positions shown in Fig. 2), which is chosen based on the distance between the two vacancies and energetic preference. By introducing a pair of V_{Zn} , the GB suffers only slight distortion, and the bond length contraction does not exceed 0.1 Å, as the local strain is balanced by the stable ring structure. The altered coordination numbers and presence of a greater number of dangling bonds facilitate the formation of vacancy pairs. To enumerate this, the atomic arrangement of the relaxed GB along with the positions of

FIG. 4. The E^f of V_{Zn} and V_O for different charge states as a function of the E_F . (a) represents the O-rich condition and (b) represents the Zn-rich condition. The zero of E_F axis corresponds to VBM. The kinks in the graph represent the charge transition.

FIG. 5. Relaxed GB in the presence of a pair of V_{Zn} . The grey and pink atoms indicate Zn and O, respectively. The V_{Zn} sites are indicated.

both vacancies in presence of periodic boundary conditions is depicted in Fig. 5. Positions of the two Zn vacancies are denoted as V_{Zn1} and V_{Zn2} , respectively. The periodically repeating image of V_{Zn1} can also be seen in Fig. 5. Since we observe that the vacancies are more easily formed at the 3-fold coordinated sites compared to the 4-fold coordinated ones, the distortion is not significant, as more open volume is available at the GB for the bonds to readjust.

We study the effect of the distance of separation between the vacancy pairs (D) to understand the aggregation tendency. The E^f of different V_{Zn} pairs in the GB with their respective D values is presented in Table I. The vacancy pairs are generally more stable at the 3-fold coordinated sites, compared to those with 4-fold coordination. In particular, the vacancy pairs V_7 - V_{11} and V_7 - V_{15} that are located at the neck sites with 3-fold coordination are the most stable ones. In addition, the second vacancy prefers to be a first neighbor, as bond relaxations have already occurred in the vicinity of the first vacancy. It is seen that the E^f of a vacancy pair increases as D increases, indicating that there exists a driving force for the vacancies to remain at the GB. In bulk ZnO, the aggregation of V_{Zn} is found to be less likely, due to the high migration barrier of about 1.4 eV, which requires high annealing temperatures to mobilize the vacancies.²⁷ Despite the observation that the defects can be stabilized with lesser energy at the GB than in the bulk-like regions, the migration barriers may be high as well to prevent vacancy aggregation. However, the special bond arrangements at the GB attract the vacancies, as defects can easily form at under-coordinated atomic sites in the GB.³¹

TABLE I. Zn vacancy pairs, separation between them (D), E^f , and maximum local magnetic moment obtained for the O atom in the vicinity of V_{Zn} .

Vacancy pair	D (Å)	E^f (eV)	Maximum local magnetic moment of O (μ_B /atom)
V_7 - V_1	2.38	4.35	0.58
V_7 - V_5	3.13	4.86	0.49
V_7 - V_3	3.47	4.05	0.56
V_7 - V_{15}	5.28	3.87	0.60
V_7 - V_{11}	6.01	3.90	0.68
V_7 - V_{13}	8.15	5.12	0.53
V_4 - V_{12}	11.23	5.55	0.58

B. Magnetism

No spin polarization is observed from either the point defect-free GBs or from introduction of a single V_{O} at both the GB and at the bulk-like region. Furthermore, we introduce a V_{O} pair to explore the possibility of producing magnetism via an increased anion vacancy concentration, obtaining zero spin polarization. On the other hand, introducing V_{Zn} at the GB induces magnetic moments on the nearest neighbor O atoms, whereas the magnetic moments on Zn atoms are negligible. To visualize the magnetism induced by V_{Zn} , we plot the spin density distribution at the GB for the stable V_{Zn} (Fig. 6). Difference between the majority and minority spin densities is calculated and indicated by iso-surfaces near V_{Zn} and at the vacancy center. The iso-surfaces show extended tails in the immediate vicinity of the vacancy. It can be seen from Fig. 6 that the effect of spin polarization induced by V_{Zn} is not limited to the nearest neighbor O atoms and extends to several O atoms near and at the GB. In addition, we find that the under-coordinated O atoms created by the neutral V_{Zn} are easily polarized and the magnetic moments are not symmetrically distributed among O atoms due to the different spatial arrangement of atoms at the GB. The local moments of the O atoms in the vicinity of V_{Zn} range from 0.3 to $0.68 \mu_B$ /atom. These O atoms with unsatisfied valence have dangling bonds and give rise to residual spin polarization due to the unpaired electrons. Hence, the O atoms that possess dangling bonds are magnetized more easily compared to other O atoms. Such magnetism is the characteristic of a d^0 semiconductor, as it is induced by the cation vacancy due to the spatial local character of the $2p$ states of the nearest anion sites around/near the defect center.^{11,36,37} In contrast, the magnetic moment of the O atoms surrounding the V_{Zn} in the bulk-like region is smaller and limited to the nearest neighbor atoms. This emphasizes the role of cation vacancies at the GBs in promoting the FM observed in TM or RE-doped ZnO.¹¹⁻¹⁵

To further investigate the possibility of RT ferromagnetic coupling originating from the GB, we calculate the energy difference (ΔE) between the ferromagnetic and antiferromagnetic (AFM) states for the two vacancy configurations and shown in Table II. The exchange coupling energy difference between the two vacancies (V_{Zn1} and V_{Zn2}) is defined as

$$\Delta E(V_{\text{Zn1}} - V_{\text{Zn2}}) = E(V_{\text{Zn1}\uparrow}V_{\text{Zn2}\downarrow}) - E(V_{\text{Zn1}\uparrow}V_{\text{Zn2}\uparrow}), \quad (2)$$

FIG. 6. Spin density of GB with the most stable V_{Zn} . The grey and pink atoms indicate Zn and O, respectively.

where the arrows represent spin-up and spin-down states, respectively. A positive value of ΔE indicates that FM is favored over AFM and vice versa. ΔE is calculated for neutral as well as for +1 and +2 charge states and presented in Table II. Holes are introduced by reducing the total number of electrons in the system. The removal of one and two electrons represents the injection of one and two holes into the system, respectively.^{22,23} We have also tested electron injection by increasing the total number of electrons; however, no enhancement in the FM is observed. It is well established that defect-induced FM requires the band edge hybridization with the defect bands near the E_F . This, in turn, facilitates the magnetic exchange coupling between the host carriers and defect states. Hole injection enhances the hybridization of states near VB by moving the E_F towards the VBM, thus, enhancing the magnetic coupling.³⁸ On the other hand, increasing electron carrier density is expected to move the E_F away from the VBM, into the conduction band,³⁹ reducing the hybridization near the E_F whereby no ferromagnetic enhancement can take place. We find that weak ferromagnetic coupling is favored for the neutral charge state for both configurations, with small energy differences ($\Delta E < 30$ meV). However, the introduction of a hole enhances

the ΔE significantly, favoring strong ferromagnetic coupling between the vacancies. We observe that ΔE increases with double positive charge (155 and 187 meV for V_7 - V_{11} and V_7 - V_{15} , respectively) compared to single charge. This energy difference is sufficient to stabilize FM against thermal fluctuations, since $\Delta E > 30$ meV is the minimum required to establish ferromagnetic coupling at RT⁴⁰ (especially as the E^f shows that presence of holes increases the stability of vacancy pairs). Interestingly, the total magnetic moment of the GB supercell also increases with the introduction of holes into the system. Although no change in the magnitude of the maximum local magnetic moment is observed with the increase in V_{Zn} concentration, the net magnetic moment of the system increases from ~ 3 to $4.5 \mu_B$ due to the presence of increased hole carriers, as can be seen from Table II. The increase in the concentration of V_{Zn} and holes at the GB raises the local hole concentration at the anion sites, shifting the E_F towards the VBM. As a result of this collective phenomenon, hybridization of O $2p$ and Zn $3d$ states near E_F increases, enhancing the ferromagnetic exchange interactions. This indicates that RTFM can be obtained in ZnO with cation vacancies located at the GB in ZnO. The results of E^f show that V_O^{+2} is more stable than V_{Zn} (Fig. 4(a)) in O-rich conditions, hence, can act as a hole compensator and destroyer of FM. However, O-rich conditions are less likely to have high concentration of V_O^{+2} .³⁶ Therefore, under equilibrium conditions, RTFM can be obtained in ZnO with cation vacancies located at the GB, if the concentration of doubly charged V_O^{+2} is low enough, thus, by avoiding complete charge compensation by electrons to maintain sufficient hole concentration.

TABLE II. Separation between two vacancy pairs (D), the number of holes added, total magnetic moment of the GB supercell, and AFM-FM energy difference (ΔE).

Vacancy pair	D (Å)	Charge	Total magnetic moment of the GB supercell (μ_B)	ΔE (meV)
V_7 - V_{11}	6.01	0	3.00	10
		+1	3.53	47
		+2	4.5	155
V_7 - V_{15}	5.28	0	3.2	23
		+1	4.02	56
		+2	4.53	187

C. Electronic structure

Density of states (DOS) analysis is carried out to gain further insight in to the observed effect of the vacancies at the GB. Initially, we calculate the total density of states (TDOS) of bulk ZnO using GGA+ U method (see the top panel of Fig. 7). The TDOS shows the semiconducting and

FIG. 7. Total DOS of bulk ZnO and GB supercell. The line at zero indicates E_F .

non-magnetic nature of bulk ZnO and the obtained band gap of 2.5 eV is a significant improvement compared to the values obtained using GGA.²⁸ The TDOS for the GB supercell without any vacancies is also calculated using the GGA+ U scheme, as shown in Fig. 7 (bottom panel). The spin-up and spin-down DOS are equal with E_F positioned in the band gap, demonstrating a semiconducting and non-magnetic nature of the GB. The DOS peaks pertaining to the GB occur at different positions compared to the bulk, due to the difference in bonding characteristics. We find that the band gap calculated from the TDOS of ZnO with GB is smaller than that of bulk ZnO. The change in coordination number of the atoms (8 and 10 atom membered rings with 3 and 4 fold coordination) at the GB compared to the bulk (6 atom membered ring with 4 fold coordination) affects the band structure of the material, owing to the reduction in covalent nature and hybridization of atoms.⁴¹ The band broadening due to the irregular atomic arrangements at the GB causes this narrowing of the band

gap. Therefore, the reduced coordination number, as well as the inhomogeneous changes in bond lengths, causes the difference in band structure, compared to grain-free ZnO. Deep unoccupied states in the band gap are not found for the GB from the DOS calculations.^{42,43}

The TDOS of the GB containing single V_O and V_{Zn} (with the lowest E^f) is also calculated and presented in Figs. 8(a) and 8(b), respectively. The TDOS of V_O exhibits semiconducting properties, with symmetrical majority (spin-up) and minority (spin-down) bands, resulting in zero magnetization of the system. In contrast, the TDOS of the GB with V_{Zn} shows that the majority spins valence states are fully occupied, while the minority ones are partially occupied. Therefore, an increase in the net spin moment is observed due to the difference between the majority and minority spin densities.

Further, the projected DOS (PDOS) of O $2s$, $2p$ and Zn $4s$, $4p$, $3d$ orbitals (t_{2g} and e_g) are shown in Figs. 9(a)–9(c) for the GB containing V_{Zn} . The VBM mainly consists of O $2p$ states

FIG. 8. Total DOS of GB with V_{Zn} and V_O . The line at zero indicates E_F .

FIG. 9. Orbital resolved DOS of Zn and O atoms when V_{Zn} is present at the GB. The line at zero indicates E_F .

(Fig. 9(a)). A mixture of s and p states of Zn and O forms the conduction band minimum (CBM), whereas the contributions of the Zn $4s$ and $4p$ states are negligible, as can be seen from Fig. 9(b). It is also evident that Zn $3d$ states (t_{2g} and e_g) contribute to the VBM (Fig. 9(c)). A further analysis of the PDOS indicates that the observed magnetism arises from the O $2p$ orbitals surrounding the V_{Zn} ; however, the contributions of the O $2s$ states are negligible. The formation of two holes in the $2p$ band at the O sites surrounding the V_{Zn} is the main source of this magnetization, whereas the contributions from the Zn $4s$ and $4p$ states are negligible. Consequently, the observed magnetism is mainly due to the O p states at the top of the VB. However, there is a small contribution from the Zn $3d$ states, which can hybridize with the O p states, promoting the p - d exchange interaction.⁴⁴ The origin of magnetism from this p - d interaction can be traced back to the oxygen atomic properties. Substitutionally, doped O in solids has been shown to possess finite magnetic moments.⁴⁵ O atom contains two unpaired $2p$ electrons, leading to a net magnetic moment of $2 \mu_B$. On the other hand, the maximum local moment at the GB, possessed by the O atoms in the vicinity of V_{Zn} , is about $0.68 \mu_B/\text{atom}$. The removal of a Zn atom from the GB results in unpaired dangling bonds and the neighboring O atoms move outward from their original positions, causing a prominent Jahn-Teller type distortion. This reduces the local magnetic moment of the O atoms from the ideal value of $2 \mu_B$. However, the total spin polarization of the system increases in the presence of higher density of vacancies and/or other defects located near the GB, which enhance the ferromagnetic exchange interactions and thereby promote ferromagnetic coupling. With the introduction of more number of holes, E_F shifts into the VBM; hence, by Stoner's criterion, the spin polarization increases.⁴⁶ On the contrary, if the hole density decreases, E_F remains inside the

band gap, resulting in zero net magnetization, as obtained for the V_O .

IV. CONCLUSIONS

GBs are unavoidable structural elements in ZnO samples, irrespective of the method of preparation. They are often complex defects, and as such, can exhibit characteristics of both intrinsic and extrinsic defects. Our theoretical study demonstrates that no RTFM can be obtained from the GB without point defects. In a ZnO GB, V_{Zn} forms more easily than V_O and the presence of V_{Zn} at the GB is responsible for the experimentally observed RTFM in polycrystalline ZnO and the FM is further enhanced by the introduction of additional holes into the system. Although in p -type doping scenarios, V_O^{+2} can act as a hole compensator, FM may not be hindered in O rich conditions, as the concentration of V_O^{+2} is low enough to avoid the charge compensation. In conclusion, our study explains that the presence of point defects at the GBs plays a dominant role in the FM observed experimentally in ZnO samples.

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