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## Room Temperature Ferromagnetism in Sb doped ZnO

Cai-Qin Luo<sup>1,2\*</sup>, Si-Cong Zhu<sup>3</sup>, Chi Xu<sup>4</sup>, Shengqiang Zhou<sup>4</sup>, Chi-Hang Lam<sup>5</sup>, Francis Chi-Chung Ling<sup>2\*</sup>

<sup>1</sup>*Henan Key Laboratory of Photovoltaic Materials, Henan University, Kaifeng, China*

<sup>2</sup>*Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong, China*

<sup>3</sup>*College of Science and Key Laboratory for Ferrous Metallurgy and Resources Utilization of Ministry of Education, Wuhan University of Science and Technology, Wuhan, China*

<sup>4</sup>*Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstr. 400, 01328 Dresden, Germany*

<sup>5</sup>*Department of Applied Physics, Hong Kong Polytechnic University, Hung Hom, Hong Kong, China*

\* Corresponding author: ccling@hku.hk, luocq17@foxmail.com

### Abstract

Using first-principle calculations, the magnetic properties of the monovacancies and the Sb-related defects including  $V_{Zn}$ ,  $V_O$ ,  $Sb_{Zn}$ ,  $Sb_O$ ,  $Sb_{Zn}-V_{Zn}$  and  $Sb_{Zn}-2V_{Zn}$  are studied. It is found that the isolated  $V_{Zn}$  with the charge state of 0 and -1 can contribute to ferromagnetism in ZnO material. The substitution of Sb on O sites ( $Sb_O^0$ ) also results in magnetic property. Moreover, the  $Sb_{Zn}-2V_{Zn}$  complex is another defect having non-zero magnetic moment and energetically favours for the ferromagnetic state. The resultant density of states (DOS) and spin density distribution clearly show that the ferromagnetic interaction is majorly due to the O-p Zn-d and Sb-p states. To check this calculation, Sb-doped ZnO samples were grown by pulsed laser deposition with different Sb composition under  $P(O_2)=1.3$  Pa. SQUID study showed that all of these samples are ferromagnetic at room temperature. The variation of the saturation magnetization against the Sb composition is discussed.

### Keywords

Sb-doped ZnO, defects, ferromagnetism, SQUID

## Introduction

Extensive effort has been devoted to study dilute magnetic semiconductors (DMS) [1-4]. Many theoretical studies revealed the possibility of room temperature (RT) ferromagnetism (FM) introduced by dilute doping of magnetic ions in semiconductors, for example  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ [5],  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ [6],  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ [7],  $\text{Zn}_{1-x}\text{Co}_x\text{O}$ [8], etc. ZnO is a multi-functional material among these DMS [9]. There are many reports of RT FM observed in ZnO doped with a variety of transition metals like Co [10-15], Mn [10, 11, 16, 17], Fe [18] and Cu [19-21]. It was suggested that defects played crucial role in the intrinsic carrier mediated FM coupling [1, 17, 20, 21] and the presence of hole carrier could enhance the FM [22, 23]. It is not doubt that native defects, especially the dominant  $V_{\text{Zn}}$  and  $V_{\text{O}}$ , cannot be ruled out from the origin of RT FM. It is found that there is a correlation between the increase of  $V_{\text{O}}$  and the enhancement of ferromagnetism in Co doped ZnO [24]. The observed RT FM in Cu doped ZnO can be well interpreted by an indirect exchange model due to the presence of  $V_{\text{O}}$  and Cu impurities [25]. On the other hand,  $V_{\text{Zn}}$ , as one of the acceptors in ZnO with high concentration, can also be used to enhance ferromagnetism through increasing its concentration on purpose. Recently, strong FM was observed in undoped 2D ZnO by increasing  $V_{\text{Zn}}$  concentration to  $\sim 10^{22} \text{ cm}^{-3}$  through H-passivated (forming  $V_{\text{Zn-H}}$ )[26], saturated magnetization ( $M_s$ ) with value of 50.9 emu/g (around  $285.4 \text{ emu/cm}^3$ ) is one to five orders of magnitude higher than the other published results. The robust  $M_s$  is also comparable with conventional ferromagnetic materials. Their findings indicated that the increase of  $V_{\text{Zn}}$  related defects in ZnO material with massive grain boundaries is likely to significantly increase RT FM. The origin of RT FM in undoped ZnO was focused in our previous work[27, 28]. The experimental observed RT FM can be attributed to the  $V_{\text{Zn}}$  related defects residing on the grain surface [28], and the follow-on computational study indicated the unit cells of ZnO containing the  $V_{\text{Zn}}$ ,  $\text{O}_i(\text{oct})$  and  $2V_{\text{Zn}}-V_{\text{O}}$  in the configuration

of a-b plane and c axis energetically favors for FM state. The isolated  $V_O$  prefers non-polarized state, thus is not the root cause for RT FM in undoped ZnO [27]. However, there were also disagreements that the observed RT FM was originated from extrinsic origins like magnetic nanometer-sized transition metal clusters [29], magnetic oxide and secondary phase [30], grain boundary [31, 32], and residual spin on non-magnetic oxide nanocluster [33, 34].

Majority of the DMS study on ZnO was concentrated on transition metal doped ZnO and few was devoted to the study on doping ZnO with non-transition metals like C [35] and Li [36]. There were experimental studies reporting Sb-doped ZnO to have p-type conductivity [37, 38]. But there were also literature observing  $n^+$ -conductivity in Sb-doped ZnO [39, 40]. Theoretical study [41] showed that Sb occupying Zn-site  $Sb_{Zn}$  is donor and Sb occupying O-site  $Sb_O$  is deep acceptor and  $Sb_O$  has a higher formation energy than  $Sb_{Zn}$ .  $Sb_{Zn}-2V_{Zn}$  is a shallow acceptor having a low formation energy [41] and has been associated with the experimentally observed p-type conductivity or the defect compensating the electron carriers [39, 42]. Interestingly, there is also other explanation for the observation of p-type conductivity in Sb doped ZnO. Andrew et al [43] reported that Sb doping in ZnO nanowire can lead to stable p-type conduction due to O-doping stabilized by Sb decorated head-to-head basal planed inversion domain boundaries. The presence of Sb switches the surface polarity and also incorporates an extra O basal plane positioned at the polarity-switch node. Besides, it is also found that Sb doping may have influence on the formation of  $V_{Zn}$  on ZnO surface [44], the beneath Sb was predicted to enhance the driving force to align the vacancy pattern on surface/ or boundaries. It is reasonable to speculate the introduction of Sb in ZnO may affect the exotic physical properties like RT FM, which is the objective of the present study.

The concentration change of intrinsic defect and the presence of the acceptor defects in Sb-doped ZnO material could enhance magnetic property, and few efforts were devoted to study the influence of Sb dopant on the ferromagnetism in ZnO. In the present study, first

principle calculation was carried out to study the magnetic properties of the Sb-related defects in ZnO, namely  $\text{Sb}_{\text{Zn}}$ ,  $\text{Sb}_{\text{O}}$ ,  $\text{Sb}_{\text{Zn}}\text{-V}_{\text{Zn}}$  and  $\text{Sb}_{\text{Zn}}\text{-2V}_{\text{Zn}}$ . By using the DFT method, we examine the relaxed atomic geometry, the formation energy and the induced magnetic moment of these defects.  $\text{Sb}_{\text{O}}$  and  $\text{Sb}_{\text{Zn}}\text{-2V}_{\text{Zn}}$  in the zero charge states have non-zero magnetic moment and their ferromagnetic states are more energetic favourable than their anti-ferromagnetic states. Sb-doped ZnO samples were grown by pulsed laser deposition with their magnetic properties characterized. The experimental findings are discussed with the theoretical results.

## Methods for theoretical calculations

The total energy and electronic structure calculations were performed based on the density functional theory (DFT) as implemented in the Vienna *ab initio* Simulation Package. A spin-polarized generalized gradient approximation (SGGA) with Perdew-Burke-Ernzerhof (PBE) was adopted. A plane-wave energy cutoff of 400 eV is used for the plane-wave expansion of the electronic wave function, with a  $3\times 3\times 3$  Monkhorst-pack mesh grid as k point sampling throughout the calculations. The test calculations with denser k grid and higher cutoff energy give effective identical results. A  $3\times 3\times 2$  supercell with 72 atoms is used to build defective bulk ZnO. All atoms in the supercell were allowed to move during the structural optimization until relaxed to their equilibrium positions such that forces are converged to less than 0.01 eV/Å and the energy converged to less than  $10^{-5}$  eV/atom. The calculated bandgap of undoped ZnO is around 1.3 eV, which is smaller than that of the experimental value  $\sim 3.3$  eV. The band-gap discrepancy is commonly seen due to the failures of approximate exchange-correction functional, and no U parameter was used through the calculations.

## Experimental Methods

The undoped ZnO film and Sb-doped ZnO films with different Sb composition were grown on c-plane sapphire substrates with oxygen partial pressure ( $P(O_2)$ ) of 1.3 Pa or 0 Pa using pulsed laser deposition (PLD). The substrate temperature was kept at 350 °C during growth. The details of the growth can be found in reference [39]. The magnetic properties of the samples were characterized using the Quantum Design Superconducting Quantum Interference Device-Vibrating sample Magnetometer (SQUID). These samples have been characterized using a comprehensive approach, namely Hall effect measurement, X-ray diffraction (XRD), photoluminescence (PL), X-ray photoelectron spectroscopy (XPS) and positron annihilation spectroscopy (PAS). The results were presented in reference[39].

## Results of theoretical study

All the atoms are fully relaxed to the equilibrium position during structural optimization. It is worthy to discuss the relaxation effects for future reference. For the intrinsic point defects,  $V_O$  with +2 charge state causes the most significant displacement, the first neighboring Zn atoms move outward by 24%. The nearest Zn atoms are less displaced for the neutral and +1 state of  $V_O$ , with 12.3% and 0.3% inward shift compared with the ideal Zn-O bond length. Unlike  $V_O$ , the relaxation of  $V_{Zn}$  has no dependence on its charge state, the displacement is around 10.6%. The occupation of Sb on O sites ( $Sb_O$ ) has a tremendous effect on the nearest Zn and O atoms, which displace outward by 28% and 21% respectively. For the  $Sb_{Zn}$  with +2 and +3 charge state, the displacement for the near Zn and O atoms can be neglected. For  $Sb_{Zn}-V_{Zn}$ , the Sb atom tends to move forward to the direction of  $V_{Zn}$ . It is

interesting to note that Sb on Zn site with two near  $V_{Zn}$  ( $Sb_{Zn}-2V_{Zn}$ ) tends to form a five-fold structure. Sb atom shifts downward and the beneath O atom moves upward to shorten the bond-length, which is still 1.6% longer than the ideal bond length of Zn-O. The relaxation results have no significant difference for  $Sb_{Zn}-2V_{Zn}$  with neutral, -1 and -2 charge states.

Table I The Calculated cell parameters a, c,  $\alpha$  and  $\gamma$  for pure ZnO and Sb doped ZnO with different type of defects, c/a and cell volume are also included.

sample	Lattice parameter					Volume ( $\text{\AA}^3$ )
	a ( $\text{\AA}$ )	c ( $\text{\AA}$ )	$\alpha$ ( $^\circ$ )	$\gamma$ ( $^\circ$ )	c/a	
perfect ZnO	3.257	5.240	90	120	1.609	48.138
$V_O$	3.244	5.220	90	120	1.609	47.572
$V_{Zn}$	3.251	5.238	90	120	1.611	47.942
$Sb_O$	3.276	5.308	90	120	1.620	49.333
$Sb_{Zn}$	3.267	5.292	90	120	1.620	48.914
$Sb_{Zn}-V_{Zn}$	3.267	5.242	90	120	1.605	48.452
$Sb_{Zn}-2V_{Zn}$	3.268	5.221	90	120	1.598	48.288

The lattice parameters were calculated for the 72 atom ZnO supercell for the perfect ZnO lattice. The a and c parameters are found to be 3.257  $\text{\AA}$  and 5.240  $\text{\AA}$  respectively, which are ~0.7 % larger than the experimental values [45]. The effects of introducing a single defect of  $V_O$ ,  $V_{Zn}$ ,  $Sb_O$ ,  $Sb_{Zn}$ ,  $Sb_{Zn}-V_{Zn}$  and  $Sb_{Zn}-2V_{Zn}$  into the 72 atom ZnO supercell were also studied.

The defect concentration introduced on purpose is around  $1.1 \times 10^{21} \text{ cm}^{-3}$ , which is comparable to the value observed from experimental study [39]. The change of ZnO general parameters obtained from the theoretical results can be used to indicate the type of defects.

The resultant a and c parameters of the ZnO supercell with the addition of one such defect are tabulated in Table I. The presence of  $V_O$  or  $V_{Zn}$  with concentration of  $\sim 10^{21} \text{ cm}^{-3}$  have the effects of reducing the a-parameters to 3.244  $\text{\AA}$  and 3.251  $\text{\AA}$  and the c-parameters to 5.220  $\text{\AA}$  and 5.238  $\text{\AA}$ , respectively. The introductions of the  $Sb_O$  and the  $Sb_{Zn}$  into the supercell increase the a-parameters to 3.276  $\text{\AA}$  and 3.267  $\text{\AA}$  and the c-parameters to 5.308  $\text{\AA}$  and 5.292

Å respectively. For the  $V_{Zn}$ -related defect complexes  $Sb_{Zn}-V_{Zn}$  and  $Sb_{Zn}-2V_{Zn}$ , their presence in the supercell increase the a-parameter to 3.267 Å and 3.268 Å respectively, while their c-parameters change to 5.242 Å and 5.221 Å respectively.

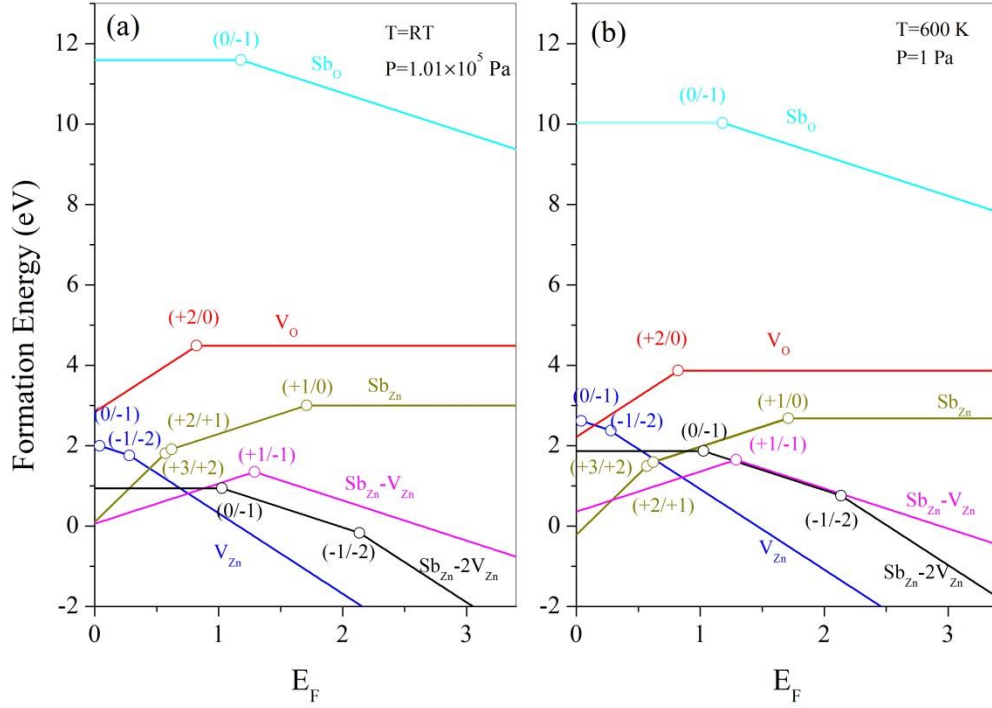


Figure 1 Formation energies of defects in Sb doped ZnO material as a function of Fermi-level, (a) standard condition, (b) condition of the interest. The Zero-point of Fermi-level corresponds to the top of valence-band. The slope represents the charge state, and only the lowest-energy state is shown. The square points in the curves indicate the transition levels in the band gap.

The concentration of the defect  $n$  is related to its formation energy under the equilibrium situation [46] via:

$$n = N_{\text{sites}} \exp\left(-\frac{E_f}{k_B T}\right) \quad (1)$$



where  $E^f$  is the formation energy,  $k_B$  is the Boltzmann constant and  $T$  is the temperature. The energy of defect formation in ZnO as function of defect species  $X$ , charge state  $q$ , and temperature  $T$  and oxygen partial pressure  $P$  is given as [47, 48]:

$$E^f(X^q) = E_{tot}(X^q) - E_{tot}(ZnO, perfect) - \sum n_i \mu_i(T, P) + q(E_V + E_F + \Delta V) \quad (2)$$

where  $E^f(X^q)$  is the formation energy of defect  $X$  in ZnO cell,  $q$  is the charge state of defect  $X$ ,  $E_{tot}(X^q)$  is the calculated total energy of a supercell having defect  $X$  in charge state  $q$ ,  $E_{tot}(ZnO, perfect)$  is the total energy of a perfect supercell without any defect.  $n_i$  is the number of atoms (type  $i$ ) that have been removed ( $n_i > 0$ ) or added ( $n_i < 0$ ) when the defect is formed.  $\mu_i(T, P)$  is the corresponding chemical potentials of the elemental species as function of temperature and oxygen partial pressure.  $E_V$  is valence-band maximum of ZnO bulk, which is defined as  $E_V = E_{tot}^{q=0}(ZnO, perfect) - E_{tot}^{q=1}(ZnO, perfect)$ .  $E_F$  is referenced to the valence-band maximum.  $\Delta V$  is added as a correction term to align the reference potential in the defective supercell with that in the perfect bulk. In present study, to line up the Fermi-level between different calculations, we align the electrostatic potentials by inspecting the potential in the supercell far from the defect and aligning it with electrostatic potential in defect-free ZnO supercell [49, 50]. Fermi level  $E_F$  is treated as a variable. The chemical potentials of the elemental species depend on the experimental growth conditions, and are treated as variables in equation (2). It is physically meaningful to place some bounds on the chemical potentials in thermodynamic equilibrium. Finnis et al [51, 52] developed an approach to obtain the oxygen chemical potential ( $\mu_O(P, T)$ ) in terms of temperature  $T$  and oxygen partial pressure  $P$ :

$$\mu_O(P, T) = \mu_O(T^0, P^0) + \Delta\mu_O^0(T) + \frac{1}{2} k_B T \log \left( \frac{P_{O_2}}{P^0} \right) \quad (3)$$

Here  $\mu_O(T^0, P^0)$  is the reference point of oxygen chemical potential at standard temperature (room temperature) and pressure (1 atm). In present study, we take the value

$\mu_{\text{O}}(T^0, P^0) = \frac{1}{2}\mu_{\text{O}_2}(T^0, P^0) = -4.19$  eV from the previously calculation [53] based on a strategy to invoke a thermodynamic cycle corresponding to formation of some oxide.  $\Delta\mu_{\text{O}}^0(T) = -1/2 [(S_{\text{O}_2}^0 - C_P^0)(T - T^0) + C_P^0 T \ln(T/T^0)]$  is the difference in oxygen chemical potential between standard temperature obtained from thermodynamic data to temperature of interest.  $S_{\text{O}_2}^0$  is the entropy of oxygen gas obtained from to thermodynamic data, and  $C_P^0$  is  $7k_B/2$ . In our previous work, Sb doped ZnO films were grown at temperature of 600 K with oxygen partial pressure  $P < 10$  Pa, which is also the condition of interest in present study. Given the circumstances, the calculated  $\Delta\mu_{\text{O}}^0(T)$  is around -0.32 eV, and the last term of Equation (2) is roughly -0.30 eV with  $T=600\text{K}$  and  $P=1$  Pa, there is no much difference (60 meV) as  $P$  increase to 10 Pa. The Zn and Sb chemical potential was derived from  $\mu_{\text{Zn}}(T, P) = \Delta H(\text{ZnO}) - \mu_{\text{O}}(T, P)$ , and  $\mu_{\text{Sb}}(T, P) = 1/2[\Delta H(\text{Sb}_2\text{O}_3) - 3\mu_{\text{O}}(T, P)]$ .  $\Delta H(\text{ZnO})$  and  $\Delta H(\text{Sb}_2\text{O}_3)$  are the obtain the enthalpies.

The growth condition plays critical role in the dopant and intrinsic defects concentration. Thus it is important to discuss the defects formation under certain circumstance. Figure 1 shows the formation energies for the defects (namely  $V_{\text{Zn}}$ ,  $\text{Sb}_{\text{O}}$ ,  $\text{Sb}_{\text{Zn}}$ ,  $\text{Sb}_{\text{Zn}} - V_{\text{Zn}}$ , and  $\text{Sb}_{\text{Zn}} - 2V_{\text{Zn}}$ ) as a function of the Fermi-level. Different charge states of the defect refer to the different slopes of the straight lines, and the turning points correspond to the ionization states of the defect in the band gap. It is noticed that the as found ionization states in Figure 1 would be slightly different from the published result [42], which may be due to the different parameters and methodology used during the calculation. For the Sb point defects,  $\text{Sb}_{\text{Zn}}$  always has lower formation energy than  $\text{Sb}_{\text{O}}$  regardless of the oxygen abundance and the  $E_{\text{F}}$  position. This phenomenon is due to the sizing effect, the  $\text{Sb}^{3+}$  ionic radius (0.62 Å) is close to that of  $\text{Zn}^{2+}$  having values of 0.74 Å, while the ionic radius of  $\text{Sb}^{3-}$  is much larger than that of  $\text{O}^{2-}$ . Consequently, the Sb dopant is thus more likely to occupy the Zn-site of the ZnO lattice. For the condition with the standard room temperature ( $T=T^0$ ) at the

standard pressure ( $P=P^0$ ),  $V_{Zn}$ ,  $Sb_{Zn}-V_{Zn}$  and  $Sb_{Zn}-2V_{Zn}$  have relatively lower formation energies than the other defects as  $E_F$  is close to the conduction band minimum (CBM).  $Sb_{Zn}$  and  $Sb_{Zn}-V_{Zn}$  have low formation energies as  $E_F$  is close to the valence band minimum (VBM). For the case of the condition of our interest in present study, the ordering of defects with very low energies has little difference compared with the standard condition irrespective of the position of Fermi-level.

Table II. Total magnetic moments per unit cell (containing 72 atoms) with different kinds of defects. The energy difference  $\Delta E$  between AFM and FM ( $E_{AFM}-E_{FM}$ ) are calculated using a twice larger unit cell (144 atoms unit cell), the separation distance is around 9.8 Å. The non-polarized states are not included.

Defect type	Charge state	Moment( $\mu_B$ )	$\Delta E$ (meV)
$V_{Zn}$	0	1.82	38
	-1	0.99	31
$Sb_O$	0	1.04	19
$Sb_{Zn}-V_{Zn}$	0	0.96	-14
$Sb_{Zn}-2V_{Zn}$	0	0.64	22
$Sb_{Zn}$	2+	0.85	-39

Table II tabulates the total magnetic moments of the supercell containing the different defects having non-zero magnetic moments. The total energy difference between the ferromagnetism (FM) and anti-ferromagnetism (AFM) states ( $E_{AFM}-E_{FM}$ ) were also calculated with the results tabulated in Table II.  $V_{Zn}$  with the charge states of 0 and -1 have magnetic moments of  $1.82\mu_B$  and  $0.99\mu_B$  respectively and their FM states are energetically favourable while compared with AFM states. This result is similar to those of the theoretical studies found in references [54]. It is noted that the energy difference ( $\Delta E = E_{AFM} - E_{FM}$ ) for  $V_{Zn}$  is around 38 meV, which is large enough to lead to room-temperature ferromagnetism.  $Sb_O^0$  also energetically favours FM ordering with a relatively small  $\Delta E \sim 20$  meV and a non-zero magnetic moment of  $1.04 \mu_B$ . The shallow acceptor  $Sb_{Zn}-2V_{Zn}$  in the neutral charge state

possesses a non-zero magnetic moment of  $0.64\mu_B$  and energetically favours the FM state ( $\Delta E \sim 20$  meV).

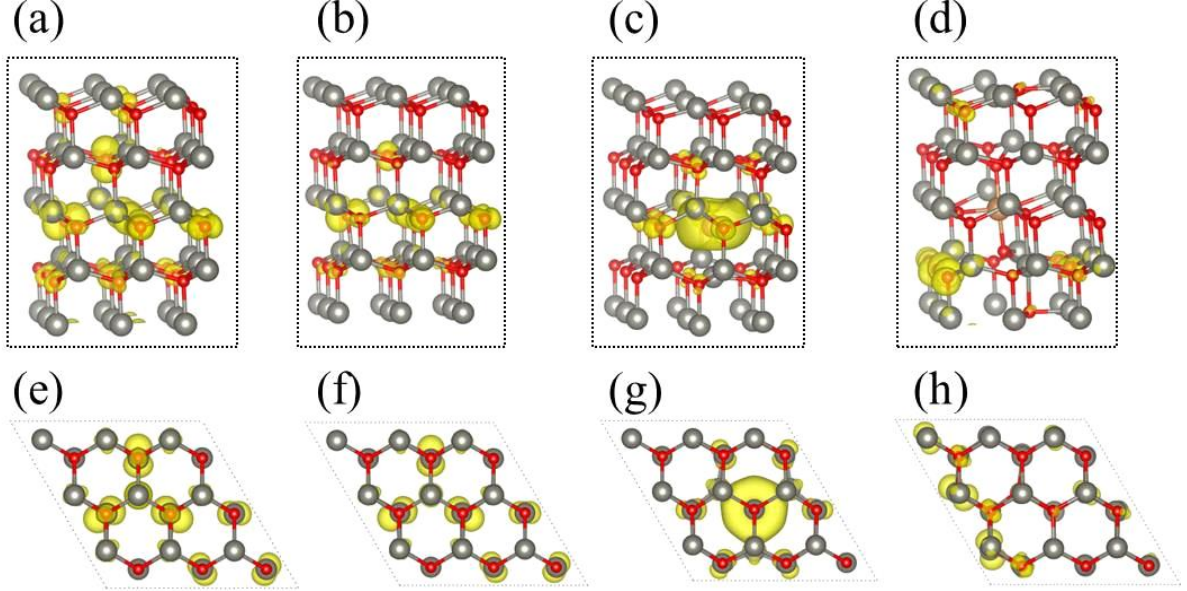


Figure 2 The side view of spin charge density distribution of ZnO with (a)  $V_{Zn}^0$ , (b)  $V_{Zn}^{1-}$ , and Sb doped ZnO with (c)  $Sb_O^0$ , (d)  $(Sb_{Zn}-2V_{Zn})^0$ ; the corresponding top view of spin charge density distribution are shown in (e)-(h).

For the defects having non-zero magnetic moment and energetically favouring the ferromagnetic state, i.e.  $V_{Zn}^0$ ,  $V_{Zn}^-$ ,  $Sb_O^0$  and  $(Sb_{Zn}-2V_{Zn})^0$ , their spin densities around the ions at 0 K in the corresponding supercell were calculated. Spin density is the difference between the spin-up and spin-down electrons. Figure 2 shows the three-dimensional iso-surface of the average spin charge density of  $0.015$  e/Å. It is clearly seen in Figure 2(a), (e), (b), (f), (d) and (h) that for the supercell containing one  $V_{Zn}$  or one  $Sb_{Zn}-2V_{Zn}$  the net magnetic moment is mainly contributed from the p electrons of the neighbouring O atom and second neighbouring O atom, and the magnetization diminishes as O atom is far from the  $V_{Zn}$ . Besides, Zn-d electrons also contribute to the magnetic moment. The contribution from Zn atoms is negligible as compared to that of O. For the case of  $Sb_O$  (figure 2(c) and (g)), the Sb substitution on O sites can also induce unpaired electron.

The total density of states (DOS) of ZnO with the defect  $V_{Zn}^0$ ,  $V_{Zn}^{1-}$ ,  $Sb_O^0$  and  $(Sb_{Zn}-2V_{Zn})^0$  are shown in figure 3 (a), (b), (c) and (d) respectively. The band gaps of the supercells are found to be underestimated, which is commonly observed in GGA functional calculation. From figure 3 (a-e), the Fermi-level passes through the spin-down states, indicating the half metallic character of the ZnO systems with these defects. However, semiconductor behaviour of undoped ZnO and Sb-doped ZnO were observed experimentally. This is due to the underestimation of the exchange splitting of the GGA functional calculation. The asymmetric DOSs for the spin-up and spin-down electrons around the Fermi-level indicate the presence of the unpaired spins, which are consistent with the spin density distribution results as shown in figure 2. The partial DOS's of the atoms contributing to the FM of the supercell containing one  $V_{Zn}^0$ ,  $V_{Zn}^-$ ,  $Sb_O^0$  and  $(Sb_{Zn}-2V_{Zn})^0$  are shown in the inserts of Figure 3(a-d) respectively. For the case of  $V_{Zn}^0$ ,  $V_{Zn}^{-1}$  and  $(Sb_{Zn}-2V_{Zn})^0$  shown in the inserts of Figure 3(a), (b) and (d) respectively, intense coupling of Zn-d and O-p states around the Fermi-level is observed. This indicates that the ferromagnetism induced by  $V_{Zn}^0$ ,  $V_{Zn}^{-1}$  and  $(Sb_{Zn}-2V_{Zn})^0$  are due to the p-d electron exchange between the Zn and O ions near the  $V_{Zn}$  defects. For the case of  $Sb_O$  shown in the inset of Figure 3(c) with the O-p, Zn-d and Sb-p states, the spin interaction is mainly due to the hybridization between the O-p and Sb-p states. The ferromagnetism induced by  $Sb_O$  is mediated through the p-p electron exchange interaction between O and Sb ions, Zn ions are also assignable for the ferromagnetism for the  $Sb_O$  case.

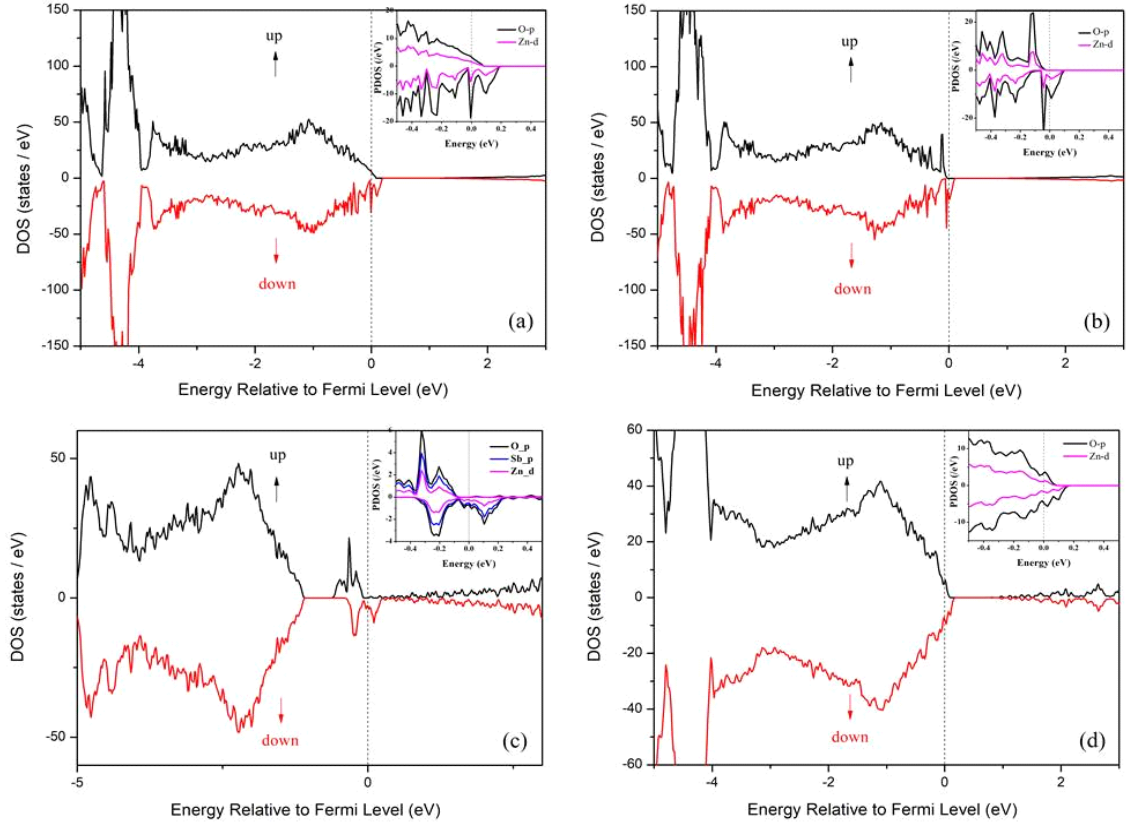


Figure 3 Total density of states of ZnO with (a)  $V_{Zn}^0$ , (b)  $V_{Zn}^{1-}$ , and Sb doped ZnO with (c)  $SbO^0$ , (d)  $(Sb_{Zn}-2V_{Zn})^0$ . The corresponding inset figure gives the partial DOS for the atoms that contribute to ferromagnetism.

## Results of experimental study

A systematic magnetic study was carried out on Sb-doped ZnO samples, which were grown with  $P(O_2) = 1.3$  Pa or 0 Pa and with different Sb composition of 0 %, 0.5 %, 1 %, 2 % and 3 %. The M-H curves in Figure 4 (a) show that all the Sb-doped ZnO samples are ferromagnetic. The M-H curve of an undoped ZnO sample grown with  $P(O_2) = 1.3$  Pa is also included in Figure 4(a). The insert of Figure 4 (a) shows the saturation magnetization against the Sb composition whereas the samples are grown with  $P(O_2) = 1.3$  Pa. The undoped ZnO film has the saturation magnetization of  $0.34 \text{ emu/cm}^3$ . The saturation magnetization (Ms) is doubled to  $0.64 \text{ emu/cm}^3$  upon the introduction of 0.5 % Sb. As the Sb composition increases

to 2 %, the saturation magnetization abruptly drops to  $0.2 \text{ emu/cm}^3$ . It then increases slightly to  $0.3 \text{ emu/cm}^3$  as the Sb composition further increases to 3 %. The reference sample (2% Sb doped ZnO film prepared with  $P(\text{O}_2)=0 \text{ Pa}$ ) was grown to investigate the oxygen influence on RT FM. It is observed from figure 4(b) that the ferromagnetism can be enhanced (the value of  $M_s$  almost doubled) as the oxygen partial pressure decrease from 1.3 Pa to 0 Pa, which indicate that chemical potential of oxygen can change the defect structure in Sb doped ZnO film, which in turn adjust the magnetic property. RT ferromagnetism was also observed in other Sb doped ZnO material, it seems that polycrystalline sample obtained by sintered [55] or using aqueous reaction [56] have much weaker FM compared with epitaxial thin films grown using physical vapor deposition [57]. It is generally accepted that the ferromagnetism of Sb doped ZnO material is assigned to  $V_{\text{Zn}}$  related defects. Doping Sb element into ZnO matrix could introduce more  $V_{\text{Zn}}$  and create a shallow acceptor defect  $\text{Sb}_{\text{Zn}}-2V_{\text{Zn}}$ . The 2p-electrons of the neighboring oxygen atoms would occupy virtual energy level and form into a spin polarized state [57]. The previous proposal to explain the origin of FM in Sb doped ZnO can be confirmed by the present theoretical calculation.

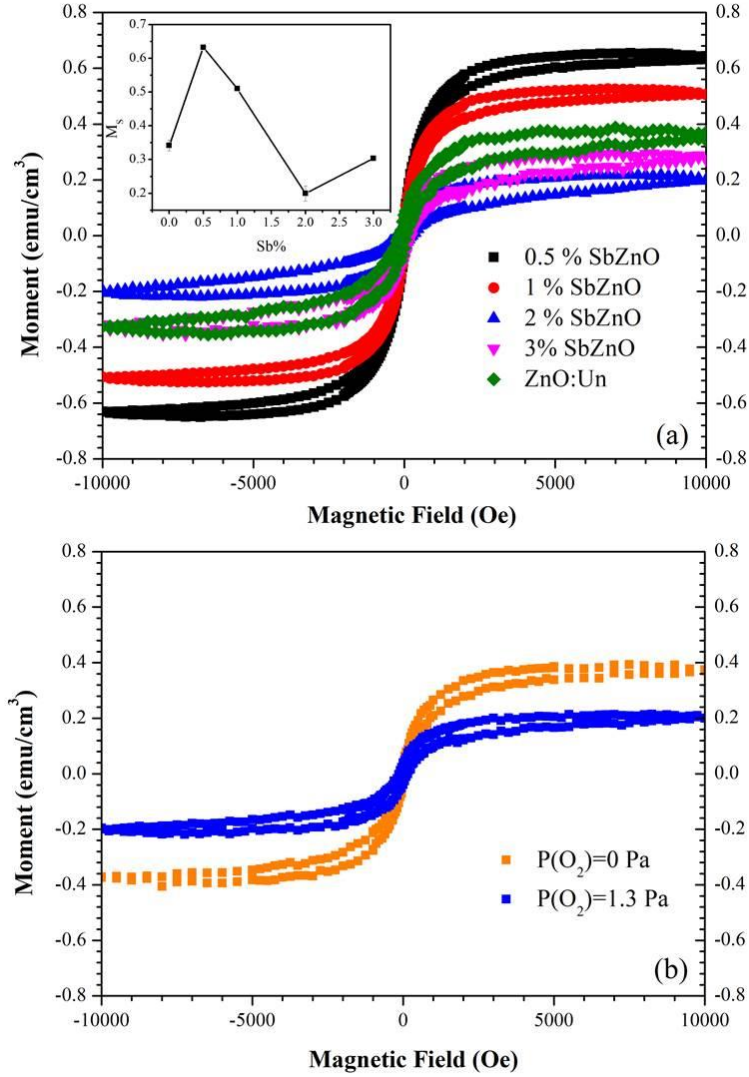


Figure 4 Room temperature  $M$ - $H$  loops of the Sb doped ZnO films: (a) the samples were grown under (a)  $P(O_2)=1.3$  Pa with different Sb concentration, the inset figure shows magnetization as a function of Sb concentration; (b) 2% Sb doped ZnO samples grown with  $P(O_2)=0$  Pa and 1.3 Pa.

## Discussion and Conclusion

In reference [39], we have performed a comprehensive and systematic study on Sb-doped ZnO samples grown with the same PLD system and methodology as the present study using a multi-spectroscopic approach, including temperature dependent Hall measurement, PAS, PL, SIMS, XRD and XPS. For the samples with Sb composition  $\leq 2\%$ , the samples were  $n^+$ -type with electron concentration  $>10^{20}$  cm<sup>-3</sup>. It is also noticed that the electron concentration increases linearly with the Sb composition, and their values were very close.



According to the present calculation, the formation energy of  $\text{Sb}_{\text{Zn}}$  is significantly smaller than that of  $\text{Sb}_{\text{O}}$  thus implying the occupation of the Sb dopant at the Zn-site rather than the O-site. First principles calculation [42] showed that  $\text{Sb}_{\text{Zn}}$  is a donor and  $\text{Sb}_{\text{O}}$  is an acceptor. The shallow donor responsible for the  $n^+$ -conductivity was thus attributed to  $\text{Sb}_{\text{Zn}}$  or the  $\text{Sb}_{\text{Zn}}$  defect complex. As the Sb composition increases to 3 %, the conductivity of the sample abruptly changed from  $n^+$  to n-type highly resistive. XRD study showed that the c-parameters of the samples with 1 % and 2 % of Sb were effectively the same as  $\sim 5.21$  Å, but increasing the Sb composition to 3 % abruptly increased the c-parameter to 5.36 Å. The increase of the c-parameter could be due to the occupation of the Sb at the O-site rather than the Zn-site. The dramatic change of the conductivity from  $n^+$  to highly resistive could be due to the formation of the  $\text{Sb}_{\text{O}}$  (or related defect complex) compensating acceptor and the drop of the  $\text{Sb}_{\text{Zn}}$  abundance. Liu et al [40] studied the MBE grown Sb-doped ZnO. A similar drop of electron concentration from  $n^+ > 10^{20} \text{ cm}^{-3}$  to  $n \sim 10^{19} \text{ cm}^{-3}$  was observed as the Sb concentration exceeded a threshold of  $\sim 4 \times 10^{21} \text{ cm}^{-3}$ , which was correlated with the abrupt increase of c-parameter revealed by XRD. The authors also attributed the shallow donor to  $\text{Sb}_{\text{Zn}}$  related defect, while the drop of the electron concentration was due to the Sb occupying the O-site rather than the Zn-site.

The present theoretical calculation shows that  $\text{V}_{\text{Zn}}$ ,  $\text{Sb}_{\text{O}}$  and  $\text{Sb}_{\text{Zn}}-2\text{V}_{\text{Zn}}$  could carry non-zero magnetization and have energetically stable FM state, whereas  $\text{V}_{\text{O}}$ ,  $\text{Sb}_{\text{Zn}}$  and  $\text{Sb}_{\text{Zn}}-\text{V}_{\text{Zn}}$  do not have stable FM state with net magnetization. Using the similar computational method, we have studied the magnetic properties of  $\text{V}_{\text{Zn}}$ ,  $\text{V}_{\text{O}}$ ,  $\text{V}_{\text{Zn}}\text{V}_{\text{O}}$ ,  $\text{V}_{\text{Zn}}-2\text{V}_{\text{O}}$  and  $\text{V}_{\text{O}}-2\text{V}_{\text{Zn}}$ . It was found that some charge states of  $\text{V}_{\text{Zn}}$ ,  $\text{V}_{\text{Zn}}\text{V}_{\text{O}}$  and  $\text{V}_{\text{O}}-2\text{V}_{\text{Zn}}$  carry non-zero magnetic moment and their FM state are energetic stable. It is noticed that all of these ferromagnetic intrinsic defects contain  $\text{V}_{\text{Zn}}$ . Moreover, it is noticed that the  $\text{V}_{\text{O}}$ -rich defects  $\text{V}_{\text{O}}$  and  $\text{V}_{\text{Zn}}-2\text{V}_{\text{O}}$  are not ferromagnetic. In the present experimental magnetic study, the

undoped ZnO sample is FM at room temperature. Its magnetic moment could be originated from the intrinsic defects  $V_{Zn}$  and the vacancy clusters  $V_{Zn}V_O$  and  $V_O-2V_{Zn}$ .

With the low level doping of 0.5 % of Sb, the saturation magnetization is doubled as compared to the undoped sample, implying that the Sb has the effect of enhancing the magnetization. For the lowly Sb-doped ZnO samples, Sb occupies the Zn-site rather than the O-site, and  $Sb_{Zn}$  or its related defect complex is the shallow donor responsible for the  $n^+$  conductivity [39]. According to the current theoretical calculation,  $Sb_{Zn}$  could carry non-zero magnetic moment but its AFM state is more energetic favourable than the FM state. The current study shows that  $Sb_O^0$  carries non-zero magnetic moment and favours for the FM state. However,  $Sb_O^0$  would not be the important contributor to the observed magnetization because  $Sb_{Zn}$  is the dominant site for Sb in this relatively low Sb composition sample. Thus, neither the  $Sb_{Zn}$  nor the  $Sb_O$  is the origin responsible for the enhanced saturation magnetization. Moreover from the current theoretical result,  $V_O$  nor  $Sb_{Zn}-V_{Zn}$  would contribute for the ferromagnetism. This implies that the  $V_{Zn}$  and  $Sb_{Zn}-2V_{Zn}$  could be the candidates contributing to the ferromagnetism.

In our previous study, Luo et al [39] observed the self-compensation phenomenon in the  $n^+$  Sb-doped ZnO samples, in which the acceptor (like  $V_{Zn}$ ) concentration is enhanced to extraordinarily high ( $\sim 10^{20} \text{ cm}^{-3}$ ) by the  $n^+$  degenerate doping. Look et al [58] and Pak et al [59] observed the similar acceptor enhancement in degenerate Ga-doped ZnO. Using PAS, Look et al [58] further showed that the acceptor was associated with  $V_{Zn}$ . The self-compensation enhancement in  $V_{Zn}$  in  $n^+$  degenerate ZnO sample is associated with the drop of the formation energy of acceptor while the Fermi level is close to the CBM (Figure 2 and Van de Walle [46]). The ZnO:Sb(0.5%) sample has saturation magnetization larger than the undoped ZnO sample. As it has just been pointed out that very high concentration of acceptor ( $\sim 10^{20} \text{ cm}^{-3}$ ), which could be  $V_{Zn}$ , was identified in the  $n^+$  Sb-doped [39]. The

increase of the saturated magnetization in the ZnO:Sb(0.5%) could be due to the abundant  $V_{Zn}$  formed because of self-compensation.

Coincidence Doppler broadening (CDB) spectroscopy is a kind of PAS which is selectively sensitive to  $V_{Zn}$  related defect. CDB spectroscopy can reveal the electronic momentum distribution in the vicinity of the Zn-vacancy in ZnO and thus able to identify the impurity decoration of the  $V_{Zn}$ . CDB study was performed on the as-grown Sb-doped ZnO samples fabricated with different Sb composition under  $P(O_2)=1.3$  Pa which was the identical set of samples of the current study, as well as the control sample Sb. The electronic momentum distribution spectrum is presented as the ratio curve which is normalized against the defect-free ZnO single crystal. A peak at zero electronic momentum was found in the Sb control sample ratio curve, and this was the fingerprint feature of positron annihilating with Sb. This feature was not found in the undoped ZnO nor the lowly Sb-doped ZnO sample with Sb=1 %, but was identified in the Sb-doped ZnO sample with Sb=2 %. This was associated to the formation of the Sb- $V_{Zn}$  defect complex, whereas positron at the  $V_{Zn}$  of this defect complex annihilated with the Sb valence electron and thus the corresponding ratio curve had the Sb feature. This implies isolated  $V_{Zn}$  exists in the undoped and the Sb(1 %) doped ZnO sample. As the Sb composition increases to 2 %,  $V_{Zn}$ -Sb type defect complex forms. Moreover, the formation of the  $V_{Zn}$ -Sb type defect complex is correlated with the introduction of the free to acceptor emission in the PL spectrum whereas the acceptor level agrees well with the theoretical value of the ionization energy of the  $Sb_{Zn}-2V_{Zn}$  acceptor [42]. It can be concluded that  $Sb_{Zn}-2V_{Zn}$  acceptor is formed as the Sb composition is raised to 2 %.

It would be worthy to discuss the origin of the drop of the magnetization as the Sb composition increases to 2 %. The observed RT FM in undoped ZnO could be originated from the  $V_{Zn}$  or the vacancy clusters  $V_{Zn}V_O$  and  $V_O-2V_{Zn}$  that carries non-zero magnetic moment and favours FM state. Doping the ZnO with 0.5 % Sb leads to the enhancement of

$V_{Zn}$  concentration because of the self-compensation effect. As  $V_{Zn}$  contributes to magnetic moment, this results in the increase of saturation magnetization from the undoped sample of  $0.34 \text{ emu/cm}^{-3}$  to the value of  $0.64 \text{ emu/cm}^{-3}$  for the 0.5 % Sb doped sample. As the Sb composition increases to 2 %,  $Sb_{Zn}-V_{Zn}$  defect complex exists in the sample rather than the  $V_{Zn}$ , which leads to the drop of the saturation magnetization to  $0.2 \text{ emu/cm}^{-3}$  because  $Sb_{Zn}-V_{Zn}$  does not favour the FM state and  $Sb_{Zn}-2V_{Zn}$  has a smaller magnetic moment as compared to  $V_{Zn}$ . As  $Sb_{Zn}$  is not ferromagnetic, the formation of  $Sb_{Zn}-2V_{Zn}$  is net effect of the removal of two  $V_{Zn}$  having high magnetic moment and forming one  $Sb_{Zn}-2V_{Zn}$  having low magnetic moment.

Magnetic study was carried out on the as-grown 2% Sb doped ZnO samples grown with different  $P(O_2)$  (1.3 Pa, 0 Pa) to investigate the influence of oxygen on the RT FM. It is found that the sample grown without extra oxygen addition shows enhanced ferromagnetism compared with the sample grown with  $P(O_2)=1.3 \text{ Pa}$ . The FM dependence on oxygen partial pressure can be assigned to the formation of  $Sb_{Zn}-2V_{Zn}$ . The hypothesis can be verified by the previous work [39], in which the electron concentration decrease with increasing oxygen pressure due to the increase concentration of  $V_{Zn}$  related defect like  $Sb_{Zn}-2V_{Zn}$ .

In conclusion, magnetic behavior of Sb doped ZnO have been studied in theoretically and experimentally. Theoretical calculation revealed that  $V_{Zn}^0$ ,  $V_{Zn}^{1-}$ ,  $SbO^0$ , and  $(Sb_{Zn}-2V_{Zn})^0$  could be the cause for the ferromagnetism in Sb doped ZnO material. Experimentally, doping ZnO with 0.5 % Sb doubles the saturation magnetization as compared to the undoped ZnO sample. This is probably due to the enhancement of  $V_{Zn}$  concentration by the self-compensation effect as the 0.5 % Sb doped ZnO has degenerate electron concentration  $\sim 10^{21} \text{ cm}^{-3}$  and  $V_{Zn}$  contribute to the ferromagnetism. As the Sb composition increases to 2 %, the saturation magnetization drops. This could be due to the formation of the  $Sb_{Zn}-2V_{Zn}$ , though it could contribute to ferromagnetism but have a lower magnetic moment as compared to  $V_{Zn}$ .

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