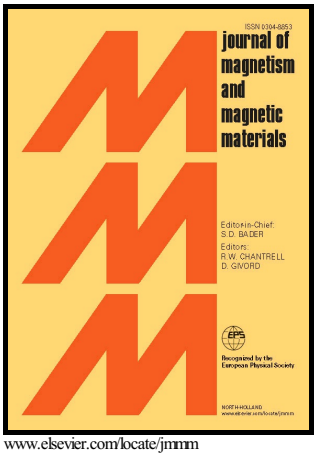

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Investigation of intrinsic defect magnetic properties in wurtzite ZnO materials

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Abstract
Theoretical and experimental investigations of the ferromagnetism induced by intrinsic defects inside wurtzite zinc oxide structures are performed using magnetic field-dependent circular dichroism (MCD-H), direct magnetization measurement (M-H) by superconducting quantum interference device (SQUID) as well as by generalized gradient density functional theory (GGA-DFT). To investigate localized magnetic moments of bulk material intrinsic defects - vacancies, interstitial atoms and Frenkel defects, various-size periodic supercells are calculated. It is shown that oxygen interstitial atoms (O_i) or zinc vacancies (Zn_v) generate magnetic moments of 1,98 и 1,26 μ_B respectively, however, the magnitudes are significantly reduced when the distance between defects increases. At the same time, the magnetic moments of oxygen Frenkel defects are large (~1.5-1.8 μ_B) and do not depend on the distance between the defects. It is shown that the origin of the induced ferromagnetism in bulk ZnO is the extra spin density on the oxygen atoms nearest to the defect. Also dependence of the magnetization of ZnO $(10\bar{1}0)$ and (0001) thin films on the positions of O_i and Zn_v in subsurface layers were investigated and it is shown that the magnetic moments of both defects are significantly different from the values inside bulk material. In order to check theoretical results regarding the defect induced ferromagnetism in ZnO, two thin films doped by carbon (C) and having Zn interstitials and oxygen vacancies were prepared and annealed in vacuum and air, respectively. According to the MCD-H and M-H measurements, the film, which was annealed in air, exhibits a ferromagnetic behavior, while the other does not. One can assume annealing of ZnO in vacuum should create oxygen vacancies or Zn interstitial atoms. At that annealing of the second C:ZnO film in air leads to essential magnetization, probably by annihilation of oxygen vacancies, formation of interstitial oxygen atoms or zinc vacancies. Thus, our experimental results confirm our theoretical conclusions that ZnO magnetization origin are O_i or Zn_v defects.

1. Introduction

In the last decade, diluted magnetic semiconductors (DMS) have attracted much attention as possible elements for future spintronics devices, where they can be ideal source of spin-polarized carriers easily integrated in modern semiconductor devices [i, ii] . Unfortunately, the temperature of ferromagnetic ordering in DMS based on III-V semiconductors such as GaAs, doped with Mn, is essentially below the room temperature, typically below 160 K. Therefore, the discovery of

non-magnetic oxides, such as ZnO [iii, iv], becoming room temperature ferromagnets (RTFM) as a result of transition metal doping (TM:ZnO) [iii, iv, v], it was one of the surprising and controversial trend in the beginning of the 21st century. Expectation that ZnO-based semiconductor magnetic elements will have important applications in semiconductor spintronics, has motivated significant research activity in recent years, see [vi]. Having a wide direct band (~3.4 eV) and large exciton binding energy (60 meV), ZnO has become one of the most promising candidates for DMS. On the other hand, ZnO has already been proposed for use in light-emitting devices [vii], varistors [viii], solar cells [ix], gas sensors [x], field emission arrays and nanoscale biosensors [xi], which paves a way to multifunctional applications.

However, the magnetic properties of zinc oxide are still subject to scientific controversy and their origins remain unclear. Besides the ferromagnetic order, the room temperature antiferromagnetism (AFM) and paramagnetism have been also observed in TM:ZnO [xii, xiii, xiv] . Recently, the RTFM was reported for non-magnetic doped ZnO and even undoped ZnO. H. Pan et al. have predicted by first-principles calculations and confirmed with pulsed-laser deposition experiments that carbon-doped ZnO exhibits ferromagnetism [xv]. The same was shown for nitrogen doping [xvi]. Later, weak RTFM was observed in undoped zinc oxide films and nanoparticles [xvii, xviii, xix], which finally gave enough ground for the conjecture, that the intrinsic defects play the crucial role in the appearance of magnetic properties. This suggestion was confirmed experimentally by comparing highly crystalline samples, obtained by molecular beam epitaxy, and defect-rich sol-gel prepared samples [xx]. Yet, there are ongoing debates on the nature of the magnetism-inducing defects: some works attribute the RTFM in undoped ZnO for Zn interstitials [xxi, xxii] and oxygen vacancies [xxiii]. Meanwhile, most of theoretical calculations propose zinc vacancies and oxygen interstitials [xxiv, xxv, xxvi] as the origin of magnetic moments. In this work, magnetic properties of intrinsic defects in bulk ZnO and thin films are studied theoretically by density functional theory (DFT) and experimentally by MCD-H and SQUID methods.

2. The calculations details and experiments.

All calculations of geometrical and electronic structures of suggested lattices were conducted with help of VASP 5.3 (Vienna Ab-initio Simulation Package) [xxvii, xxviii, xxix] quantum-chemical software package within the framework of DFT method using the plane wave basis. To reduce the number of plane waves in the basis set, the calculations were conducted with help of PAW (projector augmented wave) pseudopotentials [xxx, xxxi] under general gradient approximation (GGA) in the PBE form (Perdew-Burke-Ernzerhof) [xxxii].The k-point samplings of the first Brillouin zone (1BZ) were chosen according to the Monkhorst-Pack scheme[xxxiii]. The atomic positions were relaxed until the forces acting on each atom became smaller than 0.05 eV/A.

We have considered oxygen and zinc interstitial atoms, oxygen and zinc vacancies and Frenkel defects, consisting of a pair of the same type vacancy and interstitial atom located nearby, as intrinsic defects in the bulk wurtzite ZnO. Every periodic supercell, consisting of m×n×k unit sells, contained one fully relaxed defect. Also, thin periodic slabs having $(10\bar{1}0)$ and (0001) surfaces with O_i and Zn_v defects at different distances from the surface were investigated.

To confirm our theoretical results, we have investigated the magnetization of ZnO films by MCD-H and direct magnetization measurement by SQUID methods. For that two ZnO films doped with graphitic carbon were synthesized and then annealed at 350 °C for 1 hour in ultrahigh vacuum (1 sample) and in air (2 sample).

3. Results and discussion

Table 1 represents the magnetization for 3 various supercells consisting of 2×2×2, 3×3×3 and 4×4×3 unit cells including 32, 108 and 192 atoms respectively. Every supercell has one defect of 6 different kinds –oxygen (O_v) and zinc vacancies (Zn_v), oxygen (O_i) and zinc (Zn_i) interstitial atoms, oxygen (O_v+ O_i) and zinc (Zn_i+ Zn_v) Frenkel defects. One can see that the results of calculations of the magnetic moments of some defects depend strongly on the size of the supercell because of the difference in distances between defects in nearest periodic cell replicas. The oxygen vacancies, zinc interstitial atoms and zinc Frenkel defects have no magnetic moments for all supercells. To check a spin-orbit interaction influence on the magnetization, we have carried out calculations with the spin-orbit interaction for 2×2×2 supercell with the highest concentration of oxygen vacancies, but even in this case, the magnetic moment of O_v was not detected.

It was also found that the magnetization of oxygen interstitial atoms and zinc vacancies are greatly reduced when the distances between nearest defects are increased up to that in the 4×4×3 supercell. We can assume the totally isolated oxygen interstitial atoms would not have magnetic moments. Our results for the small 2×2×2 supercells are close to the results of [xxvii] where the authors have shown using the same package (VASP) that O_i and Zn_v have magnetic moments of 2.0 and 1.77 μ_B respectively. Unfortunately, the above-mentioned calculations were made for the 2×2×2 supercell only, so these values would not be correct if the distance between defects increases. Here we also show that the magnetization of oxygen Frenkel defects are large (~1.8μ_B) and do not changed significantly with the distance between defects.

To calculate the probability of formation of the oxygen and zinc Frenkel defects, we calculate total energies for supercells including vacancy, interstitial atom and a Frenkel defect. Then the formula (1) was used.

$$E_{Frenkel\ defect} = (E_{vac+\mathrm{int}} + E_{cell}) - (E_{vac} + E_{\mathrm{int}}), \quad (1)$$

where the total energies of different systems were calculated for the 2×2×2 supercell, the oxygen and zinc Frenkel defect energies were positive and equal to 0.61 eV and 3.44 eV, indicating that these defects are not stable for this supercell. However, for the largest supercell (4×4×3) oxygen Frenkel defect has become more stable (-0.807 eV) in comparison with individual vacancies and interstitial oxygen.

Supercell		Magnetization/unit cell					
size, number of atoms	supercell size (A) a x b x c	O_i	O_v	Zn_v	Zn_i	Frenkel O_v+ O_i	Frenkel Zn_i+ Zn_v
2x2x2 32 atoms	6.484 x 6.484 x 10.523	1.98	0	1.26	0	1.61	0
3x3x3 108 atoms	9.727 x 9.727 x 15.787	1.97	0	0.51	0	1.91	0
4x4x3 192 atoms	12.967 x 12.967 x 15.785	0.04	0	0.18	0	1.89	0

Table 1. Magnetization and parameters of some bulk ZnO supercells with defects.

To determine the cause of the supercells magnetization, we have built spin total (TDOS) and partial (PDOS) density of states for the 2×2×2 supercell with magnetic defects: O_i, Zn_v and oxygen Frenkel defect, see Figure 1.

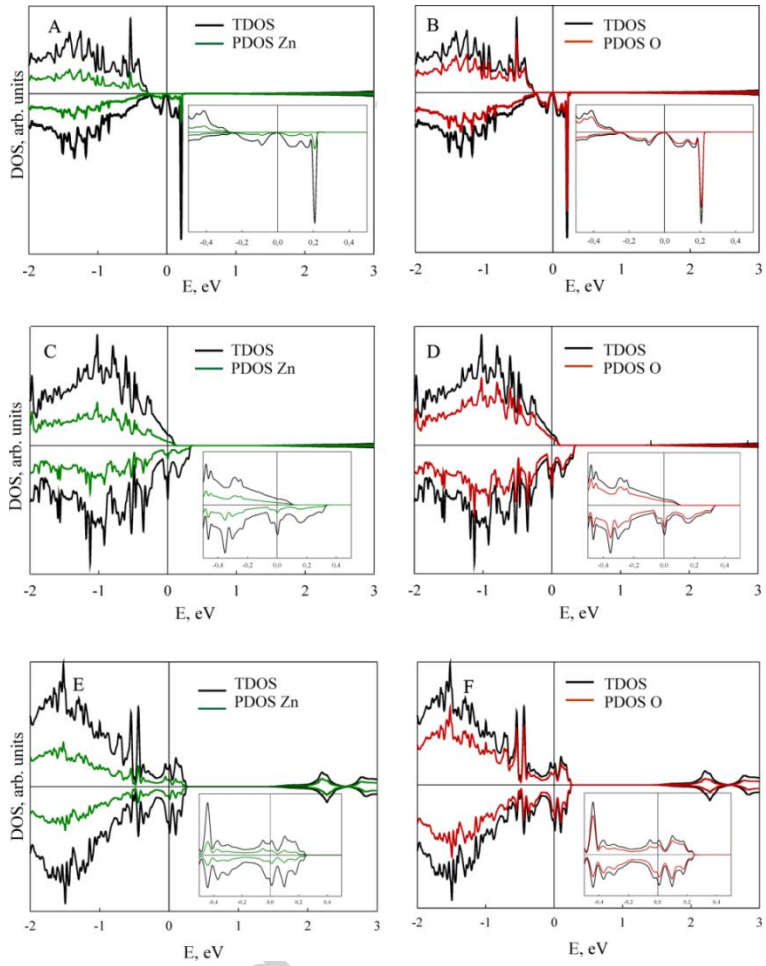
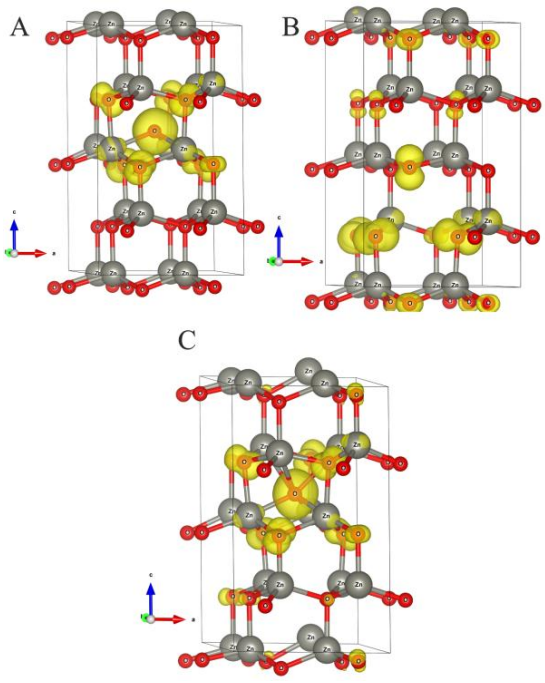


Figure 1: TDOS and PDOS of ZnO 2×2×2 supercell with different magnetic defects. A, B - with O_i defect; C, D - with Zn_v defect; E, F – with oxygen Frenkel defect. The black solid line corresponds to the TDOS, green - zinc PDOS, red - oxygen PDOS. 0 correspond to Fermi level.



One can see that in all the cases the magnetization origin is the oxygen spin density of states close to Fermi energy. In this energy region the oxygen interstitial atom states form sharper peaks in comparison with oxygen states in structure with Zn_v or oxygen Frenkel defects, so the later structures are conductive, but the structure with O_i defect is semiconductive.

Figure 2: Distribution of spin density (isosurface level is 0.005*average electron density) of ZnO 2×2×2 supercell with O_i defect (A), Zn_v defect (B) and with oxygen Frenkel defect (C).

For a clearer understanding we have built the isosurface of spatial spin density distribution, see Figure 2. Obviously, the origin of the intrinsic magnetism inside bulk ZnO with O_i, Zn_v and oxygen Frenkel defects is the extra spin density located on nearest to the defect oxygen atoms.

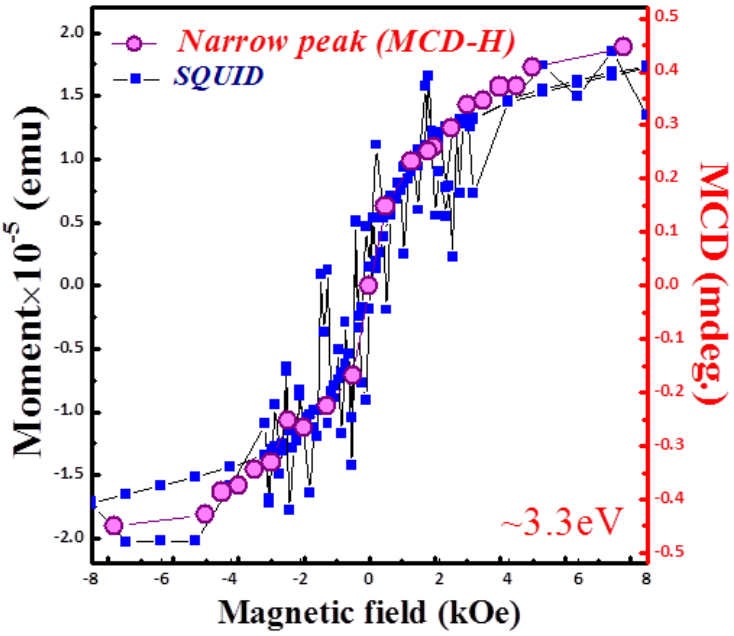
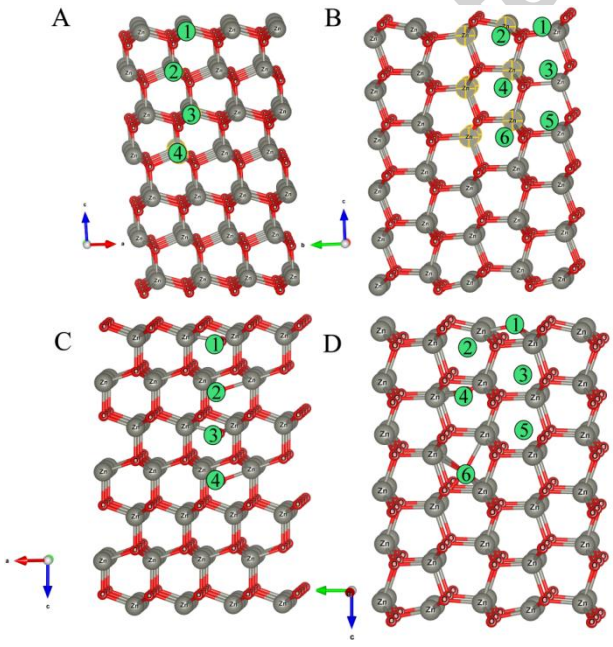


Figure 3: The MCD –H curve of the air annealed C:ZnO film together with its corresponding M-H loops.

To check our theoretical results the magnetic properties of two thin ZnO films doped with carbon were analyzed by magnetic field-dependent circular dichroism (MCD-H), direct magnetization measurement by superconducting quantum interference device (M-H). Figure 3 shows the MCD-H dependence near 3.3 eV (ZnO energy band edge) at room temperatures of the C:ZnO sample, annealed in air at 350 C. The MCD-H (red line behaves ferromagnetically and gives a saturated field of ~0.5 T, which matches the value obtained from M-H loop (blue line). This result implies that the origin of ferromagnetism is intrinsic from ZnO spin polarized semiconductor band. In comparison, for the thin film sample, annealed in vacuum (~1x10^{-2} torr), we cannot observe any ferromagnetic signal. At that one can assume annealing of C:ZnO film in vacuum should create oxygen vacancies by emission of oxygen atoms or by emission of carbon atoms occupying the oxygen positions. Also, 2ZnO + C = 2 Zn + CO_2 reaction can produce Zn interstitial atoms. Both of the possible defect types, Zn_i and O_v, are nonmagnetic according to our theoretical results. In contrast, one can assume annealing on air will reduce oxygen vacancies and even form oxygen interstitial atoms because of external oxygen atoms filling these vacancies. At the same time, the formation of Zn vacancies is also possible by Zn evaporation during annealing. So, ferromagnetism of air annealed thin films can be explained by magnetization of Zn_v or O_i defects. Consequently, these experimental results confirm our theoretical conclusions that bulk ZnO magnetization origins are intrinsic O_i or Zn_v defects.



Another purpose of the work was determination of dependences of the ZnO thin films magnetization on positions of O_i and Zn_v in subsurface layers. For that thin films having nonpolar $(10\bar{1}0)$ and polar (0001) surfaces were investigated, see Figure 4.

Figure 4: Two ZnO supercells of slabs with (0001) surface - A, C, and $(10\bar{1}0)$ surface- B, D. Positions of the oxygen interstitial atoms in different layers are shown in B, D subfigures. Positions of zinc vacancies are shown in A, C subfigures.

These surfaces were chosen as they have the lowest surface energies [xxxiv] and should be the most frequently occuring in practice. To adequately describe the $(10\bar{1}0)$ surface, a set of slabs with sizes of 1×1×n unit cells, with thickness up to n=14 atomic layers, were simulated. At that a mesh of 12×8×1 k-points was used. Approaching the thickness of 12 atomic layers, the calculated surface energy E_{surf} converged to a value of 0.9446 J/m2. Thus, for further calculations, $(10\bar{1}0)$ slabs consisting of 12 layers was used. To study O_i and Zn_v defects in this slab the supercell of size 3×3×12 (9.66×9.66×16.13 Å) was used. For 1BZ integration 3×3×1 k-points mesh was applied. Likewise, when calculating the (0001) slab it has been found that the surface energy doesn't exceed 1.0326 J/m^2 for slab thickness of 7 layers and more, so (0001) slabs consisting of 7 layers was used for further calculations. To study O_i and Zn_v defects in this slab, the supercell of size 2×2×7 (6.42×15.64×6.42 Å) was used. The k-points set was 3×3×1. After calculations of magnetic moments of the defects located in different layers inside the slab, one can see that in the (0001) slab both defect types have a magnetic moment, which significantly exceeds the values of the magnetic moments of bulk material, see Table 2. For the film with $(10\bar{1}0)$ surfaces the O_i defects are nonmagnetic from the first through the fifth layer, see Table 3.

defect layer number, see Fig.4	magnetic moment per unit cell, μ_B	
	defect O_i	defect Zn_v
1	2.888	2.892
2	2.686	2.271
3	1.944	2.262

Table 2: Calculated magnetic moments of O_i and Zn_v defects in the slab with (0001) surface.

defect layer number, see Fig.4	magnetic moment per unit cell, μ_B	
	defect O_i	defect Zn_v
1	0	1.102
2	0	1.273
3	0	0.555
5	0	0.970
6	1.758	0.930

Table 3: Calculated magnetic moments of O_i and Zn_v defects in the slab with $(10\bar{1}0)$ surface

4. Conclusions

By DFT calculations we confirm bulk wurtzite ZnO have magnetization due to localized magnetic moments of intrinsic defects - oxygen interstitial atoms, zinc vacancies and oxygen Frenkel (O_v+ O_i) defects. At that the oxygen vacancies, zinc interstitial atoms and zinc Frenkel (Zn_i+Zn_v) defects are nonmagnetic. Futhermore the magnetization of oxygen interstitial atoms and zinc vacancies are greatly reduced when the distance between nearest defects are increased up to 4x4x3 unitcells. As opposed to that, the magnetization of oxygen Frenkel defects is large (~1.8μ_B) and does not change significantly with the distance between them. By spin DOS and spin density analysis it is shown that the origin of bulk ZnO magnetization is the extra spin density on nearest to the defect oxygen atoms. To confirm our theoretical results, two C:ZnO thin films were prepared and annealed in vacuum and air. The annealed in vacuum thin film did not have a ferromagnetic behavior, while the annealed in air thin film did, as was confirmed by MCD-H and M-H measurements. It can be explained by annihilation of oxygen vacancies, formation of interstitial oxygen atoms or zinc vacancies and confirms our theoretical conclusions that the origins of bulk ZnO magnetization are O_i or Zn_v defects. Also magnetization of ZnO periodical slabs having $(10\bar{1}0)$ (0001) surfaces with different positions of O_i and Zn_v inside slabs were theoretically investigated and it was shown that the magnetic moments of both defects are significantly different from the corresponding values in bulk material and depend on the location inside the slab. The slab with (0001) surfaces shows the magnetic moments of both

defects significantly exceed the values of the defects in bulk ZnO. As opposed to this, the slab with $(10\bar{1}0)$ surface show O_i defects are nonmagnetic and Zn_v magnetic moments are half the moments of Zn_v inside (0001) slab.

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- DFT and experimental research of magnetism induced by intrinsic defects in wurtzite ZnO are performed
- O interstitials or Zn vacancies have magnetic moments which are reduced when distance between defects is increases
- O Frenkel defects have large magnetic moments which do not depend on the distance between them
- Origin of the magnetism in the bulk ZnO is the extra spin density on the O atoms nearest to the defect
- MCD measurements of ZnO film annealed in air exhibit a ferromagnetic behavior, while the other does not