

EXCHANGE INTERACTION IN ZINC OXIDE DOPED BY COBALT

M. Baranova, A. Danilyuk, V. Stempitsky
 Belarusian State University of Informatics and Radioelectronics, Minsk, Belarus

I. INTRODUCTION

ZnO has a wide range of applications which depend critically on its defect properties. Both quantum-mechanical simulation and microscopic Heisenberg model [1] are used to obtain magnetic properties. ZnO with intrinsic point defect, such as Co impurity has been investigated through chain model of magnetic ions. Exchange interaction integral was obtained for the in-plane and out-of-plane spin polarization. The computational studies reported in this article provide substantial insight about information on macroscopic magnetic properties of the material.

II. COMPUTATIONAL DETAILS

Our calculations were performed based on the density functional theory (DFT). The projector-augmented wave (PAW) [2] potentials and Perdew–Burke–Ernzerhof (PBE) [3] functional have been used. The exchange–correlation potentials was described through the local density approximation (LDA) [4] and Hubbard correction for 3d electrons of Zn ($U=7$ eV) and Co ($U=5$ eV) were employed. A cutoff energy of 500 eV and a $6 \times 6 \times 6$ k-points grids determined by a fine grid of gamma-centered method [5] in the Brillouin zone have been used. The valence electron configurations for Zn, O and Co were $3d^{10}4s^2$, $2s^22p^4$, and $3d^84s^1$, respectively. The atomic structures were relaxed until the forces on all unconstrained atoms were smaller than $0.01 \text{ eV} \cdot \text{\AA}^{-1}$.

All of calculations have been carried out using VASP (Vienna Ab-initio Simulation Package) [3, 6] wherein implemented methods described above. Structural figures and charge density drawings were produced by VESTA package [7].

The magnetic structures of exchange interactions were built by supercell, which contains $2 \times 2 \times 1$ ZnO unit cell for simulation exchange interaction of in-plane (J_{in}) and out-of-plane (J_{out}) chain impurity ions position (Fig. 1).

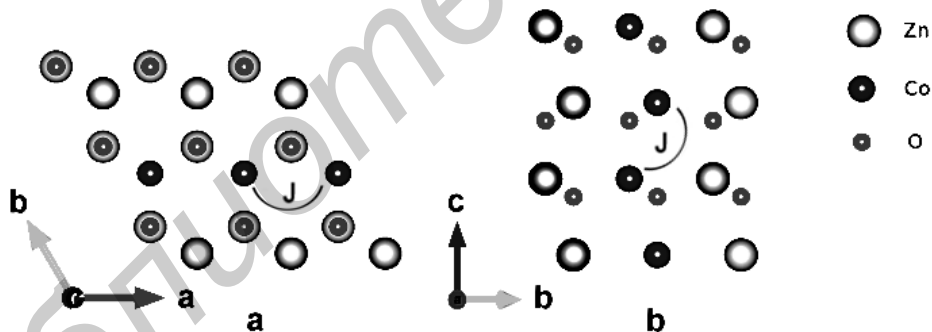


Figure 1 – Position of Co ions in the ZnO structure for modeling the exchange interaction of magnetic ions chain

The simplest and most common model of magnetism in solid states is the Heisenberg [1] model in which magnetic interaction maps through localized spin moments. The resulting classical Hamiltonian

$$(1)$$

To apply the Heisenberg model, the one of condition is dominant interaction between neighboring atoms, and neglected other interactions. Calculations were carried out at absolute zero temperature.

As the aim is the investigation of magnetic interactions we used energy differences approach in order to obtain the Heisenberg exchange parameters J_{ij} . In this approach the total energies of the zinc oxide doped by cobalt in the ferromagnetic (FM) and antiferromagnetic (AFM) are taken into account. Magnetic interactions operate only between impurity transition metal atoms. The corresponding energies of the ferromagnetic and antiferromagnetic states are

$$E_{FM} = J(S + (S_T(S_T + 1) - 2S(S + 1))) \quad (2)$$

and

$$E_{AFM} = J(2S(S + 1)) \quad (3)$$

where $S_T=2S$ for parallel spins.

In that case the energy difference in magnetic chain is

$$\Delta E = \frac{1}{2}(E_{FM} - E_{AFM}) = -\frac{J}{2}(S_T(S_T + 1)) \quad (4)$$

onto each ion. Where S_T yields 3 for Co.

III. RESULTS AND DISCUSSION

Exchange interaction integral have been obtained by quantum mechanical simulation and Heisenberg model approach (Tab. 1) for ZnO doped by Co.

Table 1 – Exchange interaction integral

Parameter	Cal. in present work	Ref.
J_{in} , meV	-1.5	-2.0 [8], -2.8 [9]
J_{out} , meV	-0.5	-1.0 [8], 0.1 [9]

It has been found that the exchange interaction of ions in-plane has antiferromagnetic ordering. Whereas, ferromagnetic state have been detected for out-of-plane ions positions. The results are in agreement with the previous calculations.

Having calculated the J_{ij} for the ground states of ZnO:Co and effective magnetic moments of cobalt ions we also calculate macroscopic magnetic parameters, such as Curie temperature (T_c), exchange constant (D , A), saturation magnetization (M_{sat}) and Bloch constant (B) (Tab. 2).

Table 2. Macroscopic magnetic parameters

J , meV	T_c , K	μ_{eff} , μ_B	D , meV \AA^2	A , J/m	M_{sat} , A/m	B , $K^{-3/2}$
1.5038, J_{in}	34.04	2.733	82.4	$1.42 \cdot 10^{-12}$	$2.88 \cdot 10^5$	$6.53 \cdot 10^{-5}$
0.471, J_{out}	10.7	2.737	25.8	$4.46 \cdot 10^{-13}$	$2.89 \cdot 10^5$	$3.7 \cdot 10^{-4}$

It is shown that the ferromagnetic state of ZnO doped by Co system is characterized by the following values for in-plane and out of plane Co position: Curie temperature lies in the range 10-34 K, exchange constant is (0.44-1.42) 10^{-12} J/m, saturation magnetization is $2.9 \cdot 10^5$ A/m, and Bloch constant ($6.5-37$) $\cdot 10^{-5} K^{-3/2}$.

III. CONCLUSIONS

In present work, we have calculated exchange integrals for Co doped ZnO using quantum-mechanical simulation and microscopic Heisenberg model. Macroscopic magnetic parameters (Curie temperature, exchange constant, saturation magnetization and Bloch constant) were obtained based on the calculated magnetic exchange interactions. The combined approach used here provides an adequate description of magnetic interactions and will be used in future study of zinc oxide doped by transition metals.

ACKNOWLEDGMENTS

This work was supported by the grants 2.53 of Belarusian National Scientific Research Program “Physical Materials Science, Novel Materials and Technologies”.

REFERENCES

- [1] I. Solovyev, M. Valentyuk, Physical Review B, 86, 2012
- [2] G. Kresse, D. Joubert, Phys. Rev. B: Condens. Matter Mater. Phys., 59, 1758–1775, 1999

- [3] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.*, 6, 15–50, 1996
- [4] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 77, 3865, 1996
- [5] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 13, 5188, 1976,
- [6] P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 50, 17953–17979, 1994
- [7] K. Momma, F. Izumi, *J. Mineral. Petrol. Sci.*, 39, 136–145, 2010
- [8] T. Chanier, M. Sargolzaei, I. Opahle, *Phys. Rev. B: Condens. Mater.*, 11, 051105, 2005
- [9] E.C. Lee and K. J. Chang, *Phys. Rev. B*, 69, 085205, 2004

ELECTRONIC PROPERTIES OF PHOSPHORENE WITH VACANCIES: AB INITIO STUDY

V. Skachkova

Belarusian State University of Informatics and Radioelectronics, Minsk, Belarus

I. INTRODUCTION

In the field of material investigation 2D-materials, such as graphene, transition-metal dichalcogenides, silicene, germanene, hexagonal boron nitride, are of great importance, because of their unique properties. One of such perspective 2D-material is phosphorene that is elemental material. Unlike graphene, it has sizable band gap from 2 (monolayer) to 0.3 eV (bulk material) [1]. Also phosphorene has high charge carrier mobility ($\sim 10^3$ cm²/V·s at room temperature) [2]. Because of puckered structure, its electronic and optical properties have strong anisotropy [3]. Because of phosphorene sensitivity to environmental conditions (oxidized in air), understanding of the mechanism of vacancy formation is important, because it leads to electronic and optical property changes during the fabrication process.

In this paper first principle calculations was carried out to investigate influence of point defects, namely mono-, two and three vacancies, on structure and electronic properties of phosphorene monolayer. The most stable kinds of vacancies were found by calculation of formation energy.

II. METHOD DESCRIPTION

Supercell, consisting of 4×4 phosphorene unit cells, with and without vacancies was constructed. Phosphorene electronic property investigations were carried out using Density Functional Theory implemented in program VASP (Vienna Ab initio Simulation Package)[4]. Calculations were performed with generalized gradient approximation (GGA), using Perdew-Burke-Ernzerhof functional (PBE). To take into account the dispersion interactions (van-der-Waals forces) DFT-D2 method of Grimme was used during geometry relaxation. Atomic core and valence electron interactions were described by augmented plane wave method (PAW). Optimization stopped when full energy difference between the last two steps was equal to $1 \cdot 10^{-6}$ eV. Cutoff energy was chosen to be 450 eV and vacuum layer thickness was equal to 17 Å to avoid layer interaction on each other. A 3×3×1 k-point mesh based on Gamma-centered Monkhorst-Pack scheme was used for all structures during structure relaxation. The vacancy formation energy E_v was calculated using equation:

$$E_v = E_t - \frac{N - 1}{N} E_b, \quad (1)$$

where E_t – supercell with vacancy full energy; N – quantity of atoms in the perfect supercell; E_b – full energy of perfect supercell.

III. RESULTS AND DISCUSSION

Results of the preliminary structure, band and DOS simulations of the initial phosphorene supercell are presented in the Table1 and on Figure 1 (a, b, c). Band gap is equal to 0.8 eV.

For monovacancy calculations atom 10 was removed (Figure 1a). One atom removing leads to three dangling bond appearance in phosphorene. Because of phosphorene flexibility, two of the dangling bonds bind to each other. And the third bond may have positive, neutral or negative charge, depending on whether it has 0, 1 or 2 electrons.

Positive-monovacancy emergence leads to changing of bond length between nearby atoms (Table 1). Besides, there is a magnetic momentum appears in the system, concentrated on 2 and 4 atoms and equal to