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DIRECT EXCHANGE INTERACTION OF COBALT CHAINS IN ZINC OXIDE: MODEL APPROACH

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Abstract. Magnetic properties of ZnO with intrinsic point defects, such as Co impurity, were calculated in the framework of quantum-mechanical Heisenberg model. Direct exchange in the chain model of magnetic ion impurities was studied, the magnetic chain was being created in (001) and (100) planes. In both cases the ground states of systems have antiferromagnetic order. Exchange interaction integrals were obtained (-1.5 and 0.5 meV). We have also calculated microscopic magnetic parameters: Curie temperature (T_{c_in} = 34.04 and T_{c_out}=10.7 K), stiffness constant (D_{in}=82.4, D_{out}=25.8 meV Å^2), saturation magnetization (M_{sat_in}=2.88×105, M_{sat_out}=2.89×105A/m), exchange constant (A_{in}=4.46× 10^{-13} and A_{out}=1.42×10^{-12} J/m), and Bloch constant (B_{in}=6.53×10^{-5} B_{out}= 3.7×10^{-4} K$^{3/2}$). For the energy of magnetic anisotropy of ZnO:Co structure it was found that the easy magnetization axis lies in (100) plane. The value of magnetic anisotropy for the whole cell is 0.06 meV. The anisotropy energy density is 5.54 × 10^4 J / m^3.

Keywords: cobalt impurity, density functional theory calculation, zinc oxide

1. Introduction

Spintronics materials should exhibit ferromagnetism with a high Curie temperature. Diluted magnetic semiconductors (DMS) and oxides are interesting for fundamental science and applications. Doped ZnO is a promising material for new technologies; in particular, it can be used in charge-carrier injectors, magnetic memory, etc. Significant advantage of these materials is compatibility with standard silicon technologies in microelectronics [1, 2]. Understanding of microscopic exchange interactions of particles is necessary for describing the magnetic properties, such as magnetic order, exchange interaction constant, magnetic anisotropy energy, etc. There are various models for describing this type of interaction [2 - 4]. The exchange interaction integral is an important parameter for magnetic materials, including doped ZnO. Knowing it, one can identify the material properties necessary for spintronics and sensorics. The first-principle simulation techniques developed allows obtain an adequate description for a system of particles having non-zero spin and calculate the exchange interaction integral.

In this study, we are not limited themselves to calculating this integral, but we also calculated the fundamental magnetic parameters and magnetic anisotropy energy that allow us to characterize nanostructures suitable for spintronics application. In doing so, we have determined the magnetic parameters of ZnO doped with transition Co metal, using *ab initio* computer simulations and microscopic Heisenberg model of magnetically ordered systems.

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2. Exchange integral of quasi-one-dimensional model and magnetic parameters

A quasi-one-dimensional magnetic microscopic model is a chain of magnetic ions in which the inside exchange interaction J is greater than the exchange interaction between the chains J'. The magnetic system becomes one-dimensional if the interaction between the chains disappears. In other words, the spins of magnetic ions predominantly interact along one direction in quasi-one-dimensional models.

Heisenberg Hamiltonian can be written in the form

$$\widehat{H} = \widehat{H}_0 + \sum_{i<j} J_{ij} \overrightarrow{S_i}\, \overrightarrow{S_j}. \quad (1)$$

To apply Heisenberg model, we assume that the interaction between neighboring atoms is dominant, and neglect other interactions. In order to obtain Heisenberg exchange parameters J_{ij}, we used the energy difference approach, in which the total energies of zinc oxide doped with cobalt in the ferromagnetic (FM) and antiferromagnetic (AFM) states are taken into account. The magnetic interactions are valid only between impurity transition metal atoms. The corresponding energies of ferromagnetic and antiferromagnetic states are

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

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

where S_T=2S for parallel spins. In this case the energy difference in a magnetic chain is

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

for each ion, where S_T equals 3 for Co.

Knowing J_{ij} for the ground states of ZnO:Co and the effective magnetic moments of cobalt ions, we can calculate the macroscopic magnetic parameters, such as

Curie temperature $T_C = 2JzS/3k(S + 1)$, (5)

stiffness constant $D = 2a^2JS$, (6)

exchange constant $A = \frac{k_s JS^2}{a}$; (7)

Bloch constant $B = (0.0587/S)(k/JS)^{3/2}$ (8)

saturation magnetization $M_{sat} = \mu_B N$. (9)

Here z is the number of nearest neighbors, S is the Co ion spin, k is Boltzmann constant; coefficient k_s, depending on the lattice type (k_s=1/4 for chain of ions); N is the number of cobalt atoms per cubic meter.

3. Computational details

ZnO crystallizes in the hexagonal wurtzite structure (space group P63mc). Due to the wurtzite structure there are two crystallographic different nearest neighbor positions: the in-plane nearest neighbor within the plane perpendicular to the hexagonal axis c and the out-of-plane nearest neighbor. In this way, two type of the supercell were used. Each supercell is formed by multiples of the primitive lattice vectors a, b, and c. The magnetic structures of exchange interactions were built by supercell, which contains 2×2×1 ZnO unit cell for simulation exchange interaction in-plane (J_{in}) and out-of-plane (J_{out}) chain impurity ion positions. The structure is shown in Fig. 1.

The calculations were based on the density functional theory (DFT). The projector-augmented wave (PAW) potentials [5] and Perdew–Burke–Ernzerhof (PBE) functional [6] were used. The exchange–correlation potentials was described through the local density approximation (LDA) [7] and Hubbard correction for 3d electrons of Zn (U= 7 eV) and Co (U= 5 eV) were employed. The cutoff energy of 500 eV and 6×6×6 *k*-point grids were determined by a fine grid of gamma-centered method [8] in the Brillouin zone. The valence electron configurations for Zn, O and Co were $3d^{10}4s^2$, $2s^2 2p^4$, and $3d^8 4s^1$, respectively. The atomic structures were relaxed until the forces on all unconstrained atoms were smaller than 0.01 eV·Å^{-1}. All the calculations were carried out at absolute zero temperature using VASP (Vienna Ab-initio Simulation Package) [6, 9]. Structural figures and charge density

drawings were produced by VESTA package [10]. Lattice relaxation has been done for a supercell which models out-of-plane and in-plane exchange interaction for FM and AFM orders. Structure parameters such as lattice constants and supercell volumes are collected in Table 1.

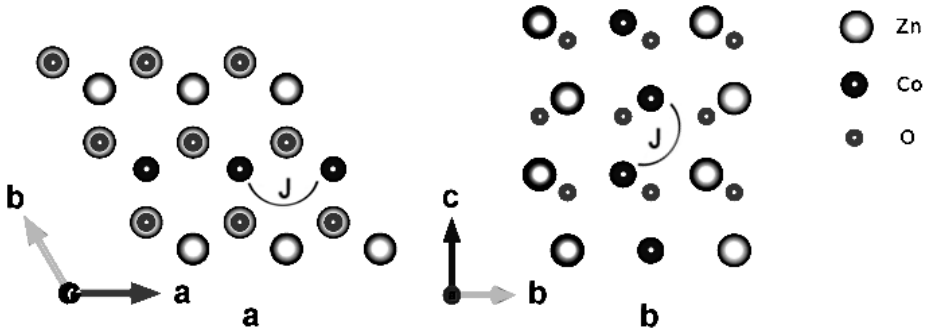

Fig. 1. Position of Co ions in ZnO structure for modeling the exchange interaction of magnetic ion chains

Table 1. Structure parameters of ZnO:Co

		a, Å	*c*, Å	V, Å^3
Out-of-plane	FM	6.3270	5.069	175.76
	AFM	6.3537	5.0942	178.09
In-plane	FM	6.3184	5.0765	175.83
	AFM	6.3130	5.0771	175.69

4. Results and discussion

Self-consistent collinear calculations were performed for determining the total system energy of FM and AFM orders and magnetic parameters (Table 2).

Table 2. Magnetic properties of ZnO:Co

		μ_B / Co_1	μ_B / Co_2	$\sum\mu_B$/a.u.	$\sum$E, eV
Out-of-plane	FM	2.74	2.74	5.83	-65.349130
	AFM	-2.73	2.73	0.00	-65.360436
In-plane	FM	2.73	2.73	5.83	-65.208385
	AFM	-2.72	2.72	0.00	-65.244477

The electronic state density for FM ordering is shown in Fig. 2. The Fermi level in the figure is shifted to zero. The upper dashed line corresponds to the electron states of spin up, and the lower solid line corresponds to the electron states of spin down. A significant asymmetry in the total density of electronic states is observed in the region from -8 to -2 eV.

Figure 3 shows the density of Co electronic states in ZnO:Co structure. The solid line corresponds to the allowed electronic states on d-orbitals, and the dashed line corresponds to the allowed electronic states on p-orbitals. The analysis of projected state densities has shown that the main contribution to the magnetic moment is made by Co ions. Accordingly the d-orbitals make a fundamental contribution to the total magnetic moment of the entire system.

As can be seen, in both out-of-plane and in-plane exchange interactions in the magnetic Co ion chain have AFM ground state. The total magnetic moment per atomic unit is 0.36 μB/a.u. which is wholly concentrated on Co impurity. The values for in-plane (J_{in}) and out-of-plane exchange (J_{out}) integrals are collected in Table 3. The results are in a good agreement with the data from the literature.

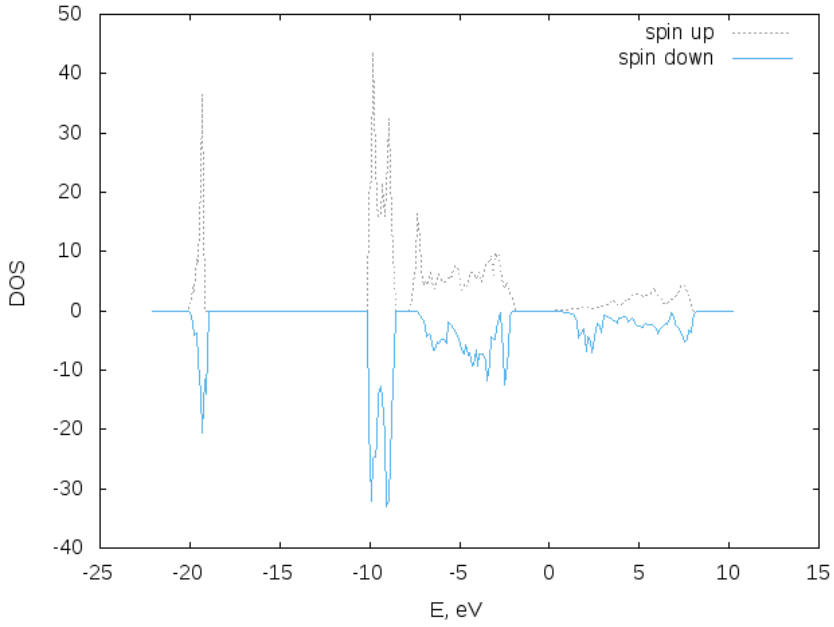

Fig. 2. Density of states ZnO:Co with FM order

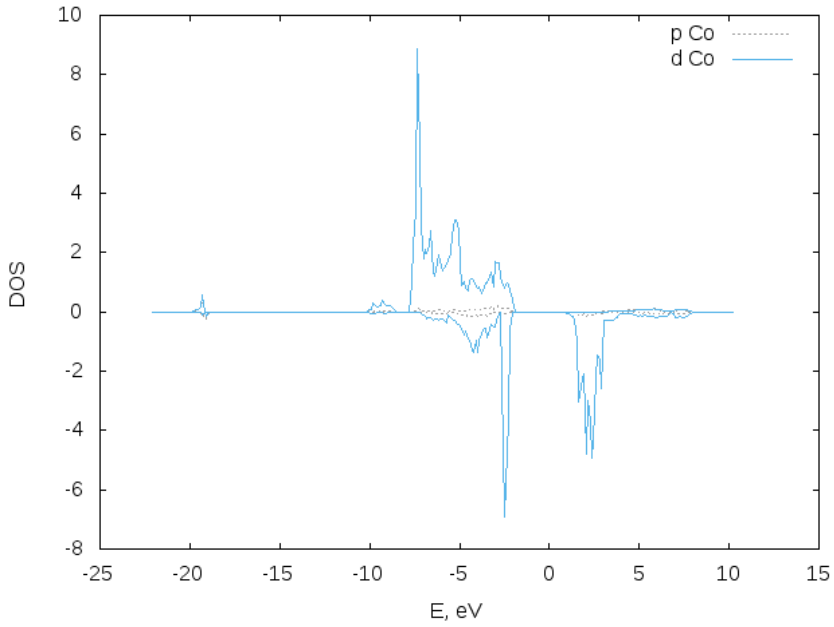

Fig. 3. Projected density of Co states with FM order

Table 3. Exchange interaction integral

Parameter	Cal. in present work	Ref.
J_{in}, meV	-1.5	-2.0 [11], -2.8 [12]
J_{out}, meV	-0.5	-1.0 [11], 0.1 [12]

It is found that in-plane nearest-neighbor magnetic exchange has antiferromagnetic ordering. Having J_{ij} for the ground states of ZnO with Co impurity and effective magnetic moments of cobalt ions, we have calculated Curie temperature (T_c), stiffness constant (D), saturation magnetization (M_{sat}), exchange constant and Bloch constant. They are given in Table 4.

Table 4. Microscopic magnetic parameters

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

It is found that the ferromagnetic state of ZnO: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 $2.9\cdot10^5$ A/m, and Bloch constant $(6.5\text{-}37)\cdot10^{-5}$ K$^{-3/2}$.

The magnetic anisotropy energy (MAE) of the ZnO:Co structure was determined using a series of quantum mechanical calculations. The calculations were performed using a supercell consisting of 2 × 2 × 1 unit cells in which two zinc atoms were replaced by a cobalt atom. The impurity concentration in this case was 12.5%.

The calculations should be carried out with great accuracy, since the difference between the two ground states with different spin orientation is of hundredths of an electron volt. For this reason, at first test calculations were performed to find optimal parameters. As a result the cutoff energy was increased by 30% and the 10×10×10 k-point grid was chosen. The convergence criterion was fulfilled when the energy difference between two consecutive calculation steps was equal to 10^{-8}.

The MAE was found in several steps. At first collinear self-consistent calculation was done Then two sets of non self-consistent calculations were performed for the magnetic moments oriented along [001] and [100] crystallographic directions with switched on spin-orbit coupling. MAE was obtained as the difference of the total energies:

$$E_{MAE}=E_{[easy]}-E_{[uvk]}. \quad (10)$$

Here $E_{[easy]}$ and $E_{[uvk]}$ is the total energy when Co spins are parallel to the easy and hard magnetization axis, respectively. The easy and hard magnetization axes were found by the lowest value of the system total energy (Table 5). The axis of easy magnetization lies in the (100) plane for the case under consideration. The value of the magnetic anisotropy of the whole cell is 0.06 meV or 0.00375 meV per atomic unit (E_{MAE}).

Table 5. Energy of magnetic anisotropy

Parameter	E, meV
$E_{[100]}$	247.47014
$E_{[001]}$	247.47008
MAE, meV	0.06
E_{MAE}	0.00375
Energy density, J/м^3	5.544×10^{4}

5. Conclusions

In present work, we have calculated exchange integrals for Co ion chains doped with ZnO using quantum-mechanical simulation and microscopic Heisenberg model. The main goal was to describe adequately direct exchange in a quasi-one-dimensional magnetic model and to obtain magnetic parameters, which can be compared with experimental data. The microscopic magnetic parameters obtained are: Curie temperature (T_{c_in} = 34.04 and T_{c_out}=10.7 K), stiffness constant (D_{in}=82.4, D_{out}=25.8 meV Å^2), saturation magnetization (M_{sat_in}=2.88×10^5, M_{sat_out}=2.89×10^5A/m), exchange constant (A_{in}=4.46×10^{-13} and A_{out}=1.42×10-12 J/m), and Bloch constant (B_{in}=6.53×10^{-5} B_{out}= 3.7×10^{-4} K$^{3/2}$).

The magnetic anisotropy energy was determined in terms of the magnetic force theorem by first principles simulation taking into account the spin-orbital interaction. It was found that the easy magnetization axis lies in (100) plane. The value of the magnetic anisotropy for the whole cell is 0.06 meV. The anisotropy energy density is 5.54×104 J / m^3. The combined approach used here provides an adequate description of magnetic interactions and will be used in the future study of zinc oxide doped by transition metals.

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