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Diluted magnetic semiconductor: structure, size and shape, and magnetic properties

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Abstract: In dilute magnetic metallic alloys, spin exchange interactions among transition metal ions at the ZnO structure cause changes in the magnetic properties of the nanocrystals depending on size and shape. The effect of size and shape on the structural and magnetic properties of semiconductors, using atomistic spin calculations, is the main topic of this study. When the size of the system decreases to a few nanometers, stability is not observed as a result of the large size. We theoretically examine the magnetic properties of CoZnO materials according to size and shape effects using the Monte Carlo method and the Heisenberg Hamiltonian VAMPIRE software package. We observe that size and shape control the magnetic disorder and temperature-dependent magnetization in Co-doped ZnO materials.

Key words: RKKY, dilute magnetic semiconductor, Monte Carlo, size effect, shape effect

1. Introduction

Dilute magnetic semiconductors (DMSs) are magnetic materials where parts of the host metal are replaced by magnetic ions of rare earth or transition metals. DMSs are key materials for spin electronics where not only the electron's charge but also its spin is used in electronic devices. They are capable of describing two important physical properties of DMSs in terms of their semiconductor and magnetic property. Two of the most important applications of these materials are semiconductor nanocrystals and DMSs [1]. Many researchers have extensively studied DMSs in the fields of solar energy conversion, synthetic inorganic chemistry, optoelectronic devices, molecular and cellular imaging, and ultrasensitive detection [2,3]. DMSs have also drawn attention both experimentally and theoretically in the development of spintronic devices, such as giant magnetoresistance and multilayer structures for the development of semiconductor spintronic materials, in the past few years [4]. DMSs belong to a new class of ferromagnets, which are formed by doping small amounts of transition metals such as Mn, Cr, Fe, Co, or Ni into GaAs, TiO_2, and ZnO semiconductors. The transition metals are combined with nonmagnetic conductors. They are identified generally as II–VI (ZnO, ZnS, ZnTe, etc.) and III–V (GaAs, InP GaN, etc.) semiconductors and transition metal alloys [5–8]. These materials have unique physical properties in spin-based electronics such as size and shape effects [9]. Studies have shown that, depending on the concentration of transition metals, DMSs can be ferromagnetic, superparamagnetic, or a spin-glass state [10–13].

$Zn_{1-x}Co_xO$ is an important material for magneto-optical devices because of the wide band gap of ZnO as well as the high thermal solubility of Co in ZnO [14]. These materials are not only important in nanoscale

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spintronic materials, but they also provide an ideal system to understand the basics related to charge (electron and holes) and spin-coupled materials. In order to get a better understanding of the shape and the size effects on DMSs, some researchers have concentrated on low-dimensional DMS nanomaterials [15]. In dilute magnetic metallic alloys, the low densities of spins are a perturbation on the Fermi liquid representing the nonmagnetic host metal ions depending on the concentration of the local moments. They are studied in dilute Kondo systems or amorphous magnetic systems with a spin-to-spin coupling mediated by the Fermi sea of conduction electrons (RKKY coupling), which often leads to spin-glass behavior [16]. The ordering of the magnetic moments in solids is mainly driven by the Heisenberg exchange interaction [17].

2. Materials and methods

In this study, we examine the magnetic behavior of Co-doped ZnO with different material sizes and shapes. Pure ZnO is usually the hexagonal wurtzite (WZ) type, which has nearly the same tetrahedral nearest-neighbor atomic coordination as the cubic zincblende (ZB) type structure [18]. In our calculations we use $a = b = 3,262\,\dot{A}$ and $c = 5,226\,\dot{A}$ lattice parameters of the WZ structure of ZnO, as shown in Figure 1. Here we simulate the magnetic behavior of Co-doped ZnO using an atomistic spin model with the Heisenberg form of exchange, describing the interaction between two spins on neighboring atomic sites.

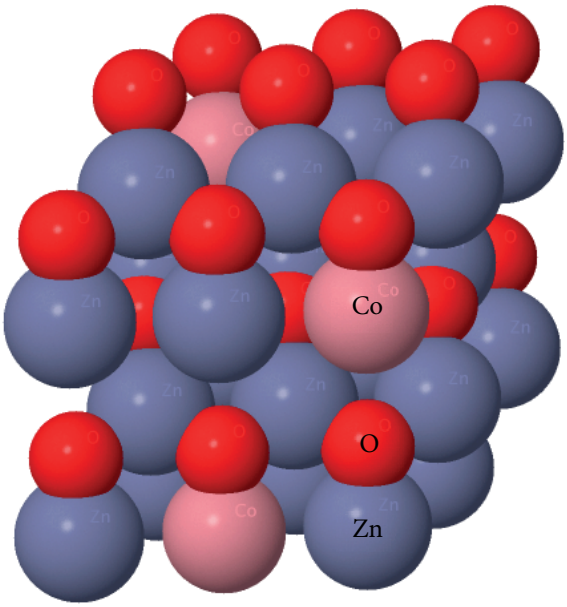

Figure 1. The crystal structure of the $Zn_{1-x}Co_xO$ wurtzite lattice. Here spheres represent Zn, O, and Co atoms.

A classical Heisenberg model generally describes the total energy of the system, which, at first, requires decoupling of the spin system to the lattice, as well as the electronic system. Thus, the classical spin Hamiltonian we study takes the following form:

$$H = -\sum_{i \neq j} J_{ij} \vec{S}_i . \vec{S}_j - d_e \left(\vec{S}_i . e \right)^2 - |\mu_s| . \vec{H}_{app} . \vec{S}_i \tag{1}$$

where d_e is the uniaxial anisotropy constant and H_{app} is the externally applied field. Here, the Heisenberg model consists of exchange interaction energy, a uniaxial energy term, and the Zeeman energy term, respectively.

$\vec{S}_i$ and $\vec{S}_j$ are the quantum mechanical spins of the atomic sites. μ_s is the atomistic spin moment and J_{ij} is the exchange integral.

In the low-medium concentration the exchange interaction is often defined by the Ruderman–Kittel–Kasuya–Yosida (RKKY) method whereby the spin-spin interactions are mediated via the conduction electrons [19–21]. Therefore, we use RKKY for the exchange interactions between the spins of the Co atoms, using the following formula [22]:

$$J_{ij} = J_{RKKY} = -j_0 e^{r/l} \left[\frac{2k_F r.Cos\left(2k_F r\right) - Sin\left(2k_F r\right)}{\left(2k_F r\right)^4} \right] \tag{2}$$

where $\mathbf{J_0 = 20 \times e^{-22}}$ J is the average exchange energy for low-medium doped transition metals [23], $\mathbf{r}$ is the distance between the two nearest neighbor spins, $\mathbf{l}$ is the damping scale of RKKY interaction due to the localization of the carriers, and the $\mathbf{e^{r/l} \cong 10}$ term originates from the limited conductivity setting of the RKKY interaction since electrons are unable to hop large distances. Because of the translational equability, the exchange integral $\mathbf{J_{ij}}$ depends only on the distance $\mathbf{r_i - r_j}$ between spins. For medium concentrations, $\mathbf{k_F \cong 10}$ is the Fermi momentum or Fermi wave vector, which depends only on the electron concentration. We calculate the magnetic behavior of CoZnO from the classical spin Hamiltonian using the VAMPIRE atomistic spin package program based on the Monte Carlo method [23].

3. Results

In light of the information explained above we simulate the magnetic properties of Co-doped ZnO using a classical Heisenberg spin model with RKKY exchange interactions between Co ions. In this study, magnetic calculations of $Zn_{1-x}Co_xO$ are performed using the VAMPIRE package depending on Co concentration. A supercell consisting of 5 × 5 × 5 and 15 × 15 × 15 unit cells is used and periodic boundary conditions are also imposed [23]. We randomly dope Co into ZnO crystals with varying sizes and shapes then examine the effects of Co doping. We simulate Co (30%)-doped ZnO material's magnetic properties via field cooling magnetization, which is usually measured in a small magnetic field as seen in Figure 2. We estimate the strength of the

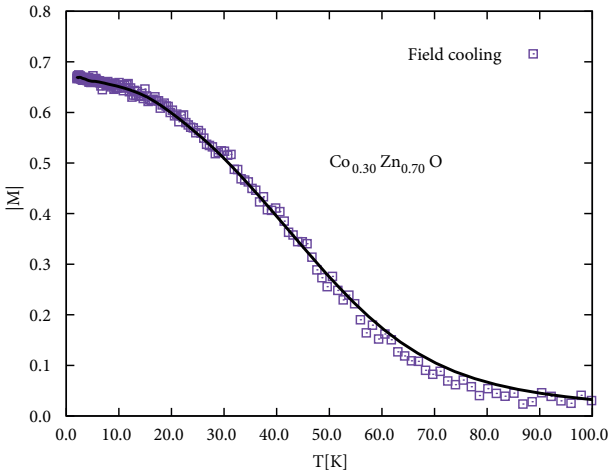

Figure 2. Field cooled magnetization curve for the $Co_{0.3}Zn_{0.7}O$ diluted magnetic semiconductor. Observed curves are obtained for the long-range ferromagnetism in the presence of ferromagnetic correlations. The system is cooled from 100 K to 0 K by 10,000 Monte Carlo steps.

interactions between the spins. This figure shows weak ferromagnetism behavior at the 1 T external applied field.

Depending on the size, shape, and temperature, the size of the system decreases to a few nanometers and stability is not observed as a result of the large size. We also simulate the magnetic behavior of materials depending on size and shape. As we can see in Figures 3 and 4, a well-defined phase transition between a ferromagnetic and a paramagnetic phase is observed. Figure 3 shows paramagnetic and weak ferromagnetic properties depending on the system size. Figure 4, on the other hand, shows unique weak ferromagnetic behavior for different crystal shapes, which are cube, cylinder, and sphere.

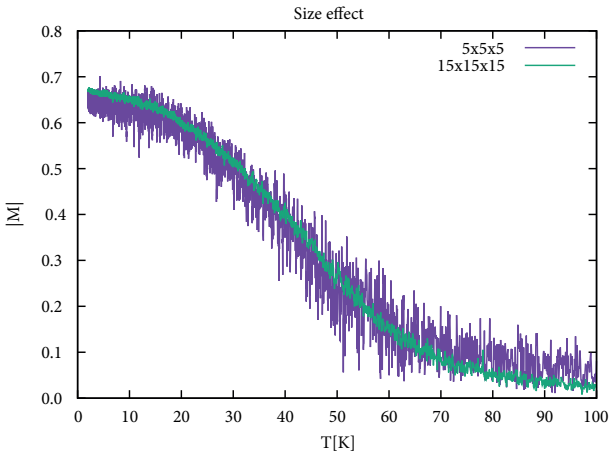

Figure 3. Temperature dependence of magnetism for different system sizes. These curves show magnetic disorder at different sizes. As the size of the system increases, the magnetic defects disappear. Temperature-dependent magnetization measurements were performed at fixed field and uniaxial anisotropy values.

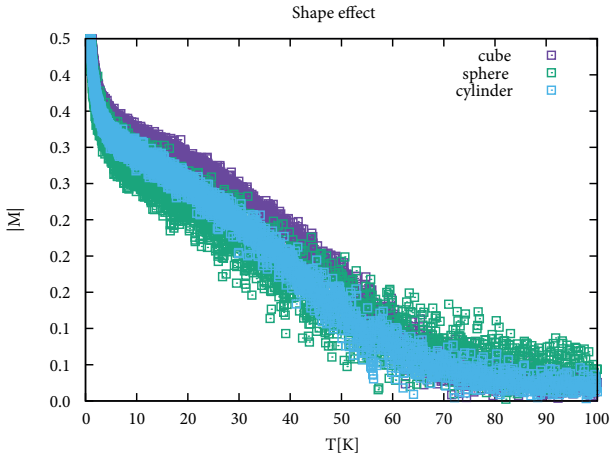

Figure 4. Different crystal structures and magnetic behaviors: cube, cylinder, and sphere. These tendencies of magnetic disorder are due to the existence of a variety of magnetic ground states commonly associated with spin-glass behaviors. The magnetic behavior of CoZnO nanoparticles was measured at various shapes from 0 K to 100 K.

4. Discussion

The aim of this work was to understand the size and shape effects on magnetic nanoparticles of Co-doped ZnO materials. We have presented the magnetic behavior of DMSs in the medium density regime using an exchange-coupling model described by the Heisenberg exchange. Magnetic exchange coupling constant calculations as a function of Co concentration in ZnO materials have been carried out based on the RKKY method, which is a suitable method to describe the mechanism of the exchange coupling. An important result of the present theory is to understand the magnetic properties of DMSs and to observe the phase behavior by introducing diluted systems.

By controlling various parameters of these materials, such as the temperature and applied external field, size and shape effects on 30% Co-doped ZnO have been studied. Because of the small size of nanoparticles, ferromagnetism effects could be an important feature of nanoparticles and their oxides. The smaller the magnetic nanoparticle, the larger the ferromagnetism effect. We anticipate that size and shape effects and doping ratio would play key roles in the further development of these particles, especially for optoelectronic applications.

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