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A Comprehensive Study of $Zn_xFe_{2-x}O_3$ Nanoparticles: Assessing Magnetic Properties for Medical Imaging (MI)

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Abstract

Diluted magnetic $Zn_xFe_{2-x}O_3$ nanoparticles are special semiconducting nanoparticles which are recognized for their magnetic properties. A theoretical examination of Zn-doped αFe_2O_3 nanostructures reveals a range of structural and property variations, offering insights into their potential applications and behavior at the nanoscale. In this regard, Heisenberg's model and Weiss molecular filed theory is used to describe the magnetic properties of $Zn_xFe_{2-x}O_3$ nanoparticles. These theorems inevitably enable to investigate the relationship between magnetic parameters, concentrations, particle size, temperature, and exchange energy. The systematic analysis of mean filed molecular theory shows that $Zn_xFe_{2-x}O_3$ exhibits mostly of superparamagnetic property and ferromagnetic ordering. The synthesis and characterization of $ZnxFe_2$-xO_3 nanoparticles are scientifically explored, with a focus on tailoring their properties, including biocompatibility, reactivity, biosensitivity, and biodegradability, for optimal performance in in vivo or in vitro applications. The result also indicates that Zn substituted αFe_2O_3 nanoparticles is a smart material by the virtue of its multiferroicity and multifunction. Besides, the ferrofluid and nanofluid characteristics of $Zn_xFe_{2-x}O_3$ nanostructures are investigated for bioelectronics and biomedical application. In addition, the impact of nanotechnology, in ensuring biomedical applications such as ferromagnetic resonance imaging is explored. Magnetic field is usually tuned for effective therapy, medical imaging, and drug delivery. By varying x=2 to 8 at %, the response of $Zn_xFe_{2-x}O_3$ nanoparticles to external Rheology such as temperature, pressure, electric fields, and magnetic fields is demystified.

Keywords: Biological (green) method, DMS, ferromagnetic fluid hyperthermia, magnetic nanoparticles, and nanotechnology

INTRODUCTION

Nanomagnetism is a broad area of study in Nanotechnology. It is a focus of life science, nanomedicine, and Spintronics. Nanomagnetism encompasses ferromagnetic materials such as magnetic nanoparticles, magnetic nano films, magnetic nanocomposite, and ferrofluid. It is widely applicable in nanogenerator, nano inductors, magnetic nanosensor, magnetic resonance imaging, and magnetic fluid hyperthermia. Nanomagnetism is central to data storage, magnetic sensors, and device technologies.

Many nanomaterials can exhibit magnetic properties. However, among these materials the most fascinating magnetic properties are observed in transition and inner transition metals, magnetic

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oxides, nanoparticles, and nanocomposite. Iron oxide nanoparticles are soft magnetic nanomaterials with high saturation magnetization and possess low coercivity.

As the size of material decreases to nano scale, a dramatic change in mechanical, electrical, optical, and magnetic property occurs. This research inculcates the nature of ferromagnetism arising from quantum size effects. For instance, bulk gold and platinum are nonmagnetic in macro scale. However, nanoparticles of Au and Pt exhibit paramagnetic, superparamagnetic, and ferromagnetic phases. These materials can be monitored by remote magnetic fields.

The property of magnetic nanoparticles in response to applied magnetic field depends on type, size, state of charge, and strength of the field applied. It also depends on the shape and geometry of surface. More importantly, the ferromagnetic property is due to unpaired electrons, quantum confinement, bound magnetic Polaron, magnetic anisotropic, RKKY interactions, double exchange interactions, and point defects.

As illustrated by Barui *et al.*, when transition metal dopant ions are ferromagnetically coupled with metal oxide, the contributions of ions to spin polarization is enhanced [1]. The study of Rubio *et al.* revealed that $Zn_xFe_{3-x}O_4$ shows hysteresis magnetization at Curie temperature 5 and 300 K [2]. However, it is predicted that $Zn_xFe_{2-x}O_3$ can exhibit a curie temperature up to 600 K. Marand *et al.* observed that ZnxFe$_3$-xO$_4$ nanoparticles prepared by Co-precipitation method exhibits super paramagnetic properties at room temperature [3]. It also exhibits high level of saturation magnetization nearly 74.60 emu/g for x=0.075. Another research by Taufiq *et al.* shows that the saturation magnetization (Ms) of $Zn_{0.2}Fe_{2.8}O_4$ powder and ferrofluid are 33.530±0.040 and 1.263±0.003 emu/g respectively [4]. On the other hand, the study of Chambers *et al.* indicates that $Ti_{0.04}Fe_{1.96}O_3$ has an average saturation magnetization of nearly 0.5 μ_B/Ti at 300 K [5]. It is also proved by Szczerba *et al.* that iron oxide nanoparticles synthesized by the co-precipitation method exhibits maximum saturation magnetization by doping the nanocrystals with non-magnetic elements such as Zinc [6]. As Zeng *et al.* illustrated, compared with Fe oxides, the saturation magnetization (M_S) of Fe/Fe_3O_4 particles (100–190 emu/g) is twice as high [7]. This means its coercivity (H_C) can be tuned from several Oe to several hundred Oe. The magnetization detected by Kasparis *et al.* shows that the maximum achievable saturation magnetization at optimum doping is 108 emu/g [8]. The study of Kumar *et al.* show that doping Fe_2O_3 with Zn at 10% exhibit maximum saturation magnetization of ~2.93×10^{-3} emu/g and coercivity of ~956 Oe [9].

As depicted by Karmakar *et al.* 2007, $ZnFe_2O_4$ spinal ferrite exhibit a phase transition from ferromagnetic to paramagnetic above 450 K [10]. Mihalache *et al.* had detected super paramagnetic states in nanocomposite of ZnO/$ZnFe_2O_4$ that find applications in gas sensors, magnetic (Nano) sensors, and antibacterial agents [11]. Earlier researches of Ramesh *et al.* show that the ferromagnetic ordering observed in $Zn_xFe_{2-x}O_3$ is due to doping conditions and anisotropic effects [12]. However, Wei *et al.* revealed, compared to single-phase samples, $Zn_{0.96}Fe_{0.04}O$ exhibits strong ferromagnetism at a Curie temperature, 400 K [13]. Besides, Darchevill *et al.* reasoned out the synthesis route and influence of its parameters on the magnetic properties of particles [14]. Photoluminescence study of Maibam *et al.* show that RTFM is attributed to the bound magnetic Polaron that arises from a singly ionized oxygen Vacancy [15].

Magnetic nanoparticles involve both the flow of electrons and spins. This makes them special nanomaterials in spintronics devices which involve both flow of electron and storage. Applying magnetic field helps to assemble the nanoparticles in dilute suspension. It also allows the determinations of dispersion and agglomeration with help of DLVO theory. The Figure 1 demonstrates the multiferroic and multifunctional properties of $Zn_xFe_{2-x}O_3$ nanoparticles. The multiferroicity arises from the fact that $Zn_xFe_{2-x}O_3$ exhibits all ferromagnetic, ferroelectric, and piezoelectricity.

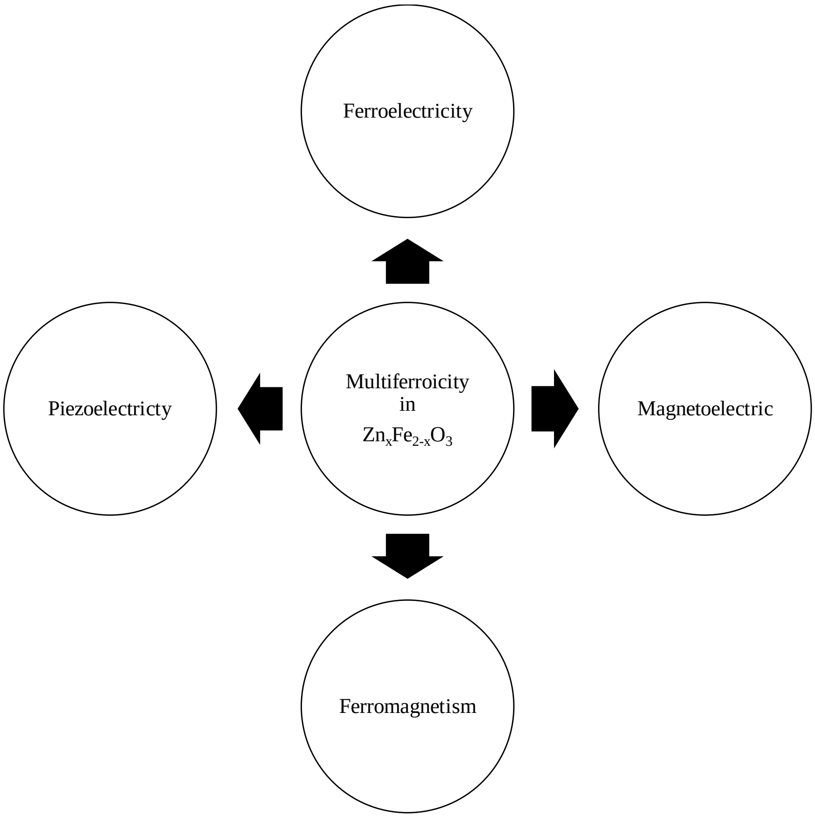

Figure 1. Multiferroicity in $Zn_xFe_{2-x}O_3$.

The research into magnetic oxide nanoparticles is getting greater attention due to its applications in various sectors. This is due to the fact that Zn doped iron oxide nanoparticles can easily interact with human and animal body tissues, act as sensor for detecting organic matters such as glucose, bio-organism, and a cell labels. More essentially, the comprehensive study of Zn doped iron oxide ($Zn_xFe_{2-x}O_3$) nanoparticles is emphasized. Iron-containing nanocomposite like $Zn_xFe_{2-x}O_3$ nanoparticles are important for biomarkers, immunoassays, immunosensors, and medical imaging devise.

3D Heisenberg Model

Werner Karl Heisenberg is a German theoretical scientist and lived from 1901 to 1976. Heisenberg had formulated theoretical models for describing mean energy, critical points, and phase transitions in magnetic systems. The possible energy states of a system of identical particles depend on the total spin system. The singlet and triplet states of the system are determined by Heisenberg models. Hence, the Hamiltonian of the system is determined by applying 3D Heisenberg Model.

$$H = -2J\sum_{i > j} S_i S_j \tag{1}$$

Where, J is the exchange integral. The factor 2 is introduced since the summation on i>j to avoid the double counting.

$$\begin{aligned} J > 0; &\quad \text{Ferromagentism} \\ J < 0; &\quad \text{Antiferromagnetism} \end{aligned} \tag{2}$$

If J>0, the spins lowers its energy so that the alignment is parallel and ferromagnetic ordering is maintained. However, if J<0, the spins increase their energy, so the alignment of spin is antiparallel so that antiferromagnetic state is established. Elemental Zn is diamagnetic. However, when substituted in the Iron oxide crystal matrix, it contributes for the overall magnetic properties of $Zn_xFe_{2-x}O_3$ nanoparticles. Zn substituted iron oxide nanoparticles exhibit both attractive and repulsive interaction when subjected to magnetic field.

Mean field Theory

In the mean field or molecular field theory, spontaneous magnetization is the second order phase transition. In the absence of external magnetic field, the Hamiltonian of a system of particles in electric interaction does not contain spin operators. However, when the systems of particles are exposed to external magnetic field it produces net magnetic moment and causes Zeeman energy splitting. In the molecular field approximation, the relation between the energy and external magnetic field are related by:

$$H = -\vec{\mu} B_{eff} \tag{3}$$

$$H = g\mu_B S_I \vec{B}_{eff} \tag{4}$$

$$\vec{B}_{eff} = \frac{2}{g\mu_B} \sum_{ij} J_{ij} S_j \tag{5}$$

In the Weiss Molecular field approximation, we can replace S_i with its thermal average$\langle S \rangle$.

$$\vec{B}_{eff} = \frac{2\langle S \rangle}{g\mu_B} \left(\sum_I J_{ij}\right) \tag{6}$$

Where $\langle S \rangle$ is the mean magnetization, J_{ij} is the exchange integral in electron volts (eV), g is the Landee factor, and μ_B is the Bohr's Magnetron. This equation is applicable for identical species with average magnetization$\langle S \rangle$. Hence, by combining the above theorem, the effective magnetic field is expressed in simplified model as:

$$\langle S \rangle = \frac{M}{n_W g \mu_B} \tag{7}$$

$$\vec{B}_{eff} = \frac{2}{n_{Wg^2 \mu_B{}^2}} \left(\sum_I J_{ij}\right). M \tag{8}$$

$$\boldsymbol{\eta} = \frac{\mathbf{2Z}}{\mathbf{n_{Wg^2 \mu_B{}^2}}} \mathbf{J} \tag{9}$$

The total exchange energy, $\sum_{\mathbf{I}} \mathbf{J_{ij}} = \mathbf{ZJ}$, and $\boldsymbol{n_w}$ is the Weiss molecular field constant. An arbitrary constant, $\boldsymbol{\eta}$ is expressed in terms of exchange energy. Exchange interaction (J) arises from the Pauli Exclusion Principle and coulomb interaction. The number of nearest number or coordination number (Z) for a single-phase rhombohedra structure of $Zn_xFe_{2-x}O_3$ is 12. In addition, the Landee factor, g for Fe is 2.1. Substituting this constant, effective magnetic field is reduced to the following form:

$$\vec{B}_{eff} = \eta . M \tag{10}$$

Where, η is constant in mean field approximation theory. A parameter that characterizes a ferromagnetic substance is magnetic susceptibility, χ_C given by:

$$\chi_C = \frac{\mu_O \mu_B{}^2}{K_B (T - T_{c)}} x_i \tag{11}$$

Where, μ_o is the permeability of free space, μ_B is the Bohr magnetron, $K_B$is the Boltzmann constant, and T_c the Curie temperature. We then define the Curie constant, C as:

For the superparamagnetic states, the inverse spin flip frequency is given by:

$$\tau = \tau_o exp\left(\frac{\Delta^{\pm}}{K_B T}\right) \tag{12}$$

Where, $\tau_o{}^{-1} = 1\text{GH}$ which is ferromagnetic resonance frequency [16]; $exp\left(\frac{\Delta}{K_B T}\right)$ is the Boltzmann probability, and $\Delta^{\pm} = \Delta + \mu_O mH\cos\theta$.

The effect of magnetic field is to alter the direction of spin magnetic moments. In the absence of magnetic field, the spin magnetic moments are non-uniform and distributed evenly. However, applying magnetic field will make the alignment of spin moments in the same directions giving rise to strong magnetism. This property is a peculiar characteristic of ferromagnetic nanomaterials. In the absence of magnetic fields, electron spins are oriented randomly. However, when a sufficient magnetic field is applied, they attain ferromagnetic order.

DISCUSSION

Magnetic Phase Shift in Zn Doped Iron Oxides Nanoparticles

Doping nanoparticles can alter the biophysical properties of Nanoparticles. Controlled transition metal (TM) doping can also change the magnetic phase of Fe_2O_3 nanoparticles from paramagnetic to superparamagnetic phase. Substitution of Zn^{2+} ions at Fe site in host lattice can effectively alter the magnetic properties. Besides, at optimum Zn concentrations and Curie temperature, Zn doped iron oxide nanoparticles change from paramagnetic to ferromagnetic Phase. In the present work, we predicted the effect of parameter rather than magnetism property. $Zn_xFe_{2-x}O_3$ can be tuned to paramagnetic, super paramagnetic, ferromagnetic, and spin glass phase by controlling the strength of magnetic field applied. These properties can also be attained by varying concentration of dopant, temperature, oxygen pressure, and size of nanoparticles. Besides, substrate, synthesis roots, and quantum confinement can affect the crystal morphology and its magnetic character shown in Figure 2(a, b).

By comparing the magnetic property of $Zn_xFe_{2-x}O_3$ nanoparticles with the previous result it is possible to judge the paramagnetic-ferromagnetic phases. However, though it exhibits a shift from paramagnetic to ferromagnetic states, its magnetic behavior might vary depending on the size of dopant, anisotropic effect, quantum size effect, and external Rheology such as heating, and magnetic fields.

It is visualized that both αFe_2O_3 and Zn doped αFe_2O_3 exhibits different magnetic phases. Most dominantly, it exhibits super paramagnetic phases due to super exchange. $Zn_xFe_{2-x}O_3$ nanoparticles can form Ferro fluid which is in the super-paramagnetic state. However, the Ferromagnetic phase arises from double exchange, bound magnetic Polaron, RKKY interactions, existence of oxygen vacancies, and quantum confinements. The ferromagnetic behavior is also expected from anisotropic effects.

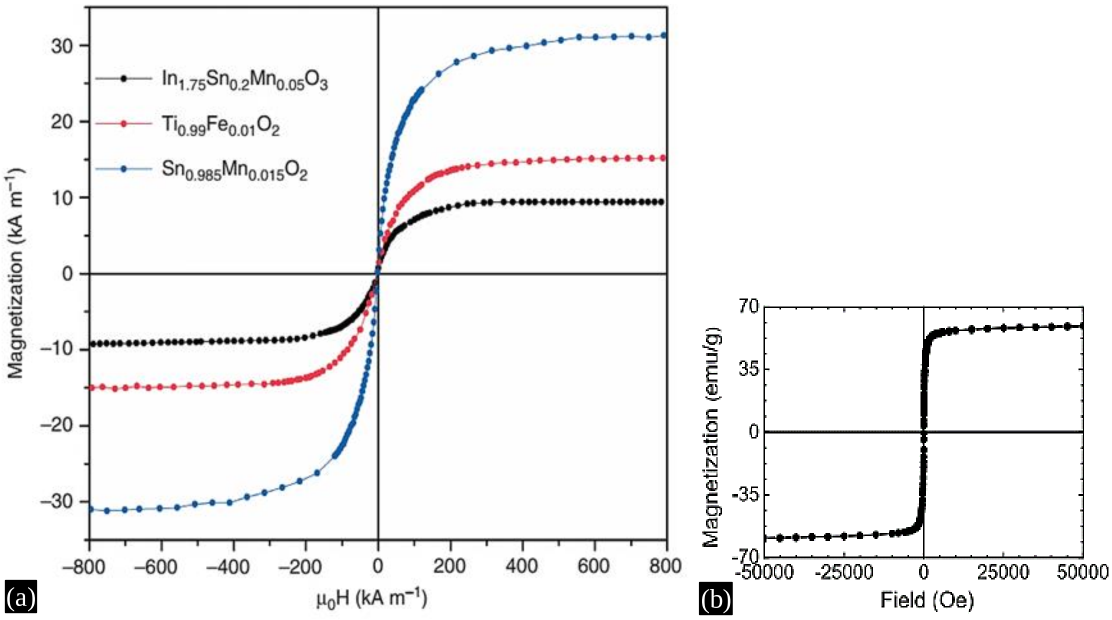

Figure 2. Magnetization curves for Transition metal doped magnetic nanoparticles [17].
(a) Magnetization curve for Transition metal doped magnetic oxide thin films;
(b) Magnetization curve for Zn substituted Fe_2O_3 nanoparticles.

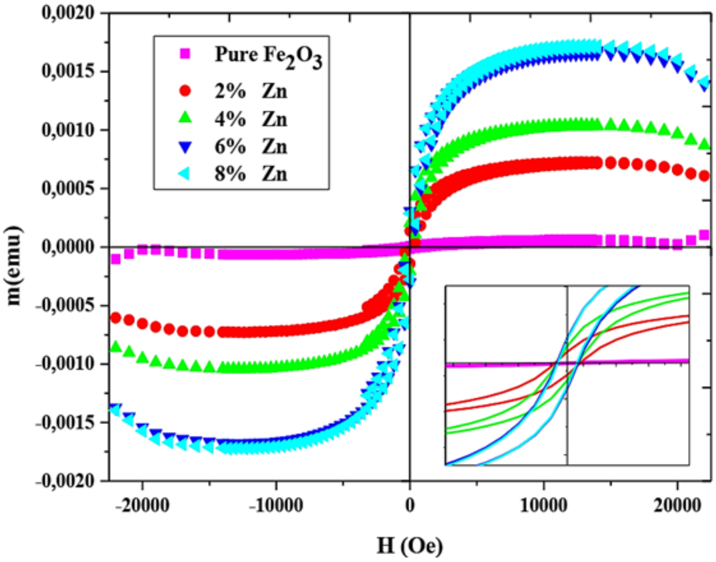

Figure 3. The relation between saturation magnetization and magnetic field [18].

Figure 3 shows that by varying the dopant ion from 2% to 8%, the relation between reduced magnetization and magnetic field strength is obtained. As Zn concentration increases in this range, transition from weak ferromagnetic to strong ferromagnetic is noticed. Doping of iron oxide with Zn ions increases the saturation magnetization largely. The magnetization mechanism of the Zn-doped Fe_2O_3 nanoparticles originates from the gas compression susceptibility parameter. Zn doping enhances Fe^{2+} to Fe^{3+} cation pairing and promotes double exchange interactions which stabilize ferromagnetic phases. It is a consequence of quantum confinement effect of $Zn_{0.4}Fe_{1.6}O_3$ nanoparticles. Besides, coercivity is directly associated with shape anisotropy. These parameters directly impact the microstructure through phase purity, cationic redistribution in the sub-lattices of the spinel, spin-canting effect, and gradient of doping inside particles. Magnetic nanoparticles such as $Zn_xFe_{2-x}O_3$ should be kept in carrier fluids for the ease of high colloidal stability, desirable saturation magnetization, and Curie temperature.

The assessment of magnetic properties shows that superparamagnetic phases control the highest percent of magnetic order. Magnetic nanoparticles such as $Zn_xFe_{2-x}O_3$ can form ferrofluid which generates heat. The heat generated by various methods stated here is hence used for fluid hyperthermia.

It is observed that as Zn dopant increases from 1 to 3%, an increase in the saturation magnetization (Ms), Remnant magnetization (Mr), and coercivity (Hc) is noticed. However, increasing the Zn dopant above 3% will decrease Mr, M_s, and $H_{c\text{ Shown}}$ in Figure 4.

Zn doping will promote magneto-optical properties by establishing tunable ferromagnetic resonance. By tuning the frequency to Larmor frequency or resonance frequency, it is possible to image cells or tissues. Hence, we can repair bone tissues or bone marrow. Functional properties of nanoparticles can be determined by leveraging their nanoscale magnetic properties. This property makes $Zn_xFe_{2-x}O_3$ nanostructures quite useful nanomaterials for cell contrast, biomarker, biosensor, and medical treatment. $Zn_xFe_{2-x}O_3$ is suitable for efficient medical imaging, therapy, diagnosis, and nano theranostics. In addition, a cell treated with iron oxide nanoparticles will promote protein aggregations. By carefully controlling the size of nanoparticles, it is possible to create fluorescent probes. This probe can emit light which is in turn useful for the purpose of biomarker. So that individual’s virus and pathogens could be detected by their wavelength. This helps to take picture of infected body cells and tissues.

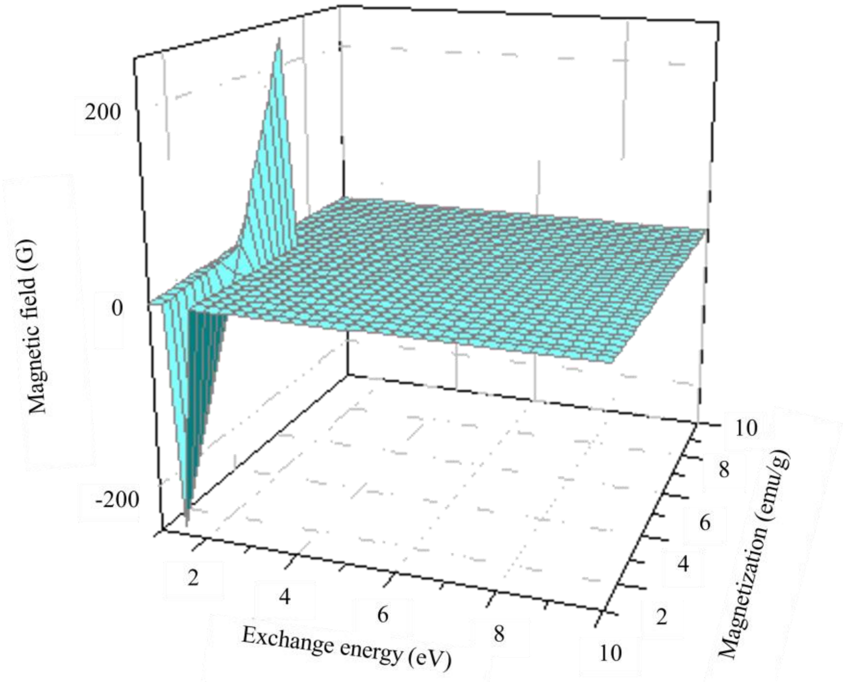

Figure 4. The relation between magnetic field exchange energy and concentration of dopant (x).

CONCLUSION

In this research, the magnetic properties of $Zn_xFe_{2-x}O_3$ nanostructures and its biomedical application is studied. Different parameters are identified for describing its physiochemical characteristics. In order to specify its functional properties, the role of nanotechnology in synthesizing, manipulating, characterizing, and utilizing $Zn_xFe_{2-x}O_3$ nanoparticles, is accounted. The physics of magnetic interactions among particles is discussed by molecular field theory and 3D Heisenberg models. These theorems are used to describe magnetic interactions via spin interactions and contribute for the expected magnetic properties. From this research, we can infer that tailoring magnetic properties by controlling external parameters enhances medical imaging using $Zn_xFe_{2-x}O_3$ nanoparticles. Moreover, tuning superparamagnetic and ferromagnetic states in $Zn_xFe_{2-x}O_3$ nanocomposite by controlled doping and magnetic field enable it promising for magnetic resonance imaging. In the future, the nanocomposite of double walled carbon nanotube/$Zn_xFe_{2-x}O_3$ is predicted for enhanced imaging and theranostics applications.

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