



Article Magnetic Properties of Gd-Doped Fe₃O₄ Nanoparticles

Iliana Apostolova ¹, Angel Apostolov ^{2,*} and Julia Wesselinowa ³

- ¹ University of Forestry, Kl. Ohridsky Blvd. 10, 1756 Sofia, Bulgaria
- ² University of Architecture, Civil Engineering and Geodesy, Hristo Smirnenski Blvd. 1, 1046 Sofia, Bulgaria
- ³ Faculty of Physics, Sofia University "St. Kliment Ohridski", J. Bouchier Blvd. 5, 1164 Sofia, Bulgaria
- * Correspondence: angelapos@abv.bg

Abstract: The magnetic properties of pure and rare earth ion-doped Fe_3O_4 nanoparticles are investigated using a microscopic model and the Green's function theory. The magnetization M_s and Curie temperature T_C are calculated depending on size, temperature and Gd doping concentration. M_s and T_C decrease with decreasing nanoparticle size and with increasing the doping concentration. The band gap energy increases with decreasing size and Gd dopants. The obtained results are in good agreement with the experimental data.

Keywords: Fe₃O₄ nanoparticles; ion doping; magnetization; curie temperature; band gap; microscopic model

1. Introduction

Nanoparticles (NPs) have received a lot of attention in the last decade due to their unique properties and wide range of applications. The magnetic behavior of magnetic NPs greatly depends on their size, shape, purity and crystal structure. Magnetite Fe_3O_4 is one of the most widely used nanomaterials for biomedical applications. Masrour et al. [1] performed self-consistent ab initio calculations and investigated the magnetic properties of bulk Fe_3O_4 . The magnetic behavior of spherical and cubic magnetite NPs are studied by Goya et al. [2], Abbad et al. [3], Sahadevan et al. [4], Wang et al. [5], Zhao et al. [6]. With decreasing particle size, the magnetic properties begin to change. Specifically, the lattice parameters are slightly enhanced [7]. Decreasing NP size leads to reduced ferrimagnetic behavior [8]. The saturation magnetization and the Curie temperature T_C of Fe_3O_4 NPs are lower than that of the bulk one [7,9]. High-saturation magnetization in small Fe_3O_4 NPs is observed by Correa et al. [10] and Nagesha et al. [11].

The magnetic properties of magnetite Fe_3O_4 can be achieved by ion doping. From a theoretical point of view, doping is a method by which the structural parameters of the crystal lattice can be drastically changed, causing shrinkage and stretching processes and changes in the nature of magnetic arrangement. Doping can significantly renormalize the magnetic phase transition temperature, magnetization, magnetic anisotropy and coercivity. The influence of rare earth (RE) doping on the magnetic properties of Fe_3O_4 NPs is investigated by Kershi et al. [12]. They observed a reduction of the magnetization and increase of the band gap. The influence of Gd doping on structural and magnetic properties of Fe_3O_4 NPs is studied by Hazarika et al. [13]. Zhang et al. [14] also considered the magnetic properties of Gd-doped magnetite NPs.

The aim of the present paper is to investigate theoretically for the first time the magnetic and optical properties of Fe_3O_4 NPs using a microscopic model and the Green's function theory.

It should be noted that the most theoretical papers consider the magnetic properties of bulk Fe_3O_4 using the density functional theory (DFT) [1,15]. The DFT is a very powerful tool in investigation of many body problems. However, DFT is mostly concerned with ground-state properties at zero temperature. In our approach, we are able to cover the



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). whole temperature regime. It is a finite temperature analysis including the entire excitation spectrum. In particular, the method allows us to study the total phase diagram, which is based on the different excitation energies realized in the system. The disadvantage of our approach consists of the consideration of collective properties from the beginning. Our basic quantities are not the "naked" electrons, but the effective spins of the underlying quasi-particles. Whereas, within DFT, all of the parameters of the system can be—at least in principle—calculated, we are forced to use additional models to find out those parameters. We are convinced that both approaches, DFT and Green's function method, are appropriate and, to a certain extent, are an alternative in describing many body systems.

2. Model and Green's Functions

Magnetite Fe₃O₄ is a ferrimagnetic mineral with a Curie temperature of $T_C = 850$ K [7]. Compounds with the structural formula Fe₃O₄ can crystallize in an inverse spinel crystal structure where the tetrahedral A sites are occupied by Fe³⁺-ions, and the octahedral B sites by an equal amount of Fe²⁺- and Fe³⁺-ions. The magnetic ions in the A and B sites interact through super-exchange interactions through an intermediate oxygen ion A-O-A, A-O-B and B-O-B, with the following relation of the exchange interaction constants: $|J_{A-B}| > |J_{B-B}| >> |J_{A-A}|$. The antiferromagnetic A-O-B interaction is the most important for the cooperative behaviour of the magnetic moments in ferrites and is of greatest intensity [16,17]. In the A and B sublattices, the exchange interactions are ferromagnetic.

By doping with RE ions, whose radius is larger than that of the iron ions (for example Gd^{3+}), they can only substitute ions at the octahedral sites. The exchange interaction between the spins of the RE and the Fe ion is mediated by a nonmagnetic oxygen ion and preserves the interaction character between the tetrahedral and octahedral sites, i.e., antiferromagnetic collinear.

The Hamiltonian, which describes the behavior of the spin subsystem of pure and Gd^{+3} -doped Fe₃O₄, is the modified Heisenberg one:

$$H_{s} = -(1-x)\sum_{ij} J_{ij}^{FeA-FeB} \mathbf{S}_{i}^{FeA} \cdot \mathbf{S}_{j}^{FeB} - (1-x)\sum_{ij} J_{ij}^{FeB-FeB} \mathbf{S}_{i}^{FeB} \cdot \mathbf{S}_{j}^{FeB}$$

- $x\sum_{ij} J_{ij}^{FeA-GdB} \mathbf{S}_{i}^{FeA} \cdot \mathbf{S}_{j}^{GdB} - x\sum_{ij} J_{ij}^{FeB-GdB} \mathbf{S}_{i}^{FeB} \cdot \mathbf{S}_{j}^{GdB}$
- $\sum_{i} D_{i}^{FeA} (S_{i}^{FeAz})^{2} - (1-x)\sum_{i} D_{i}^{FeB} (S_{i}^{FeBz})^{2} - x\sum_{i} D_{i}^{GdB} (S_{i}^{FeAz})^{2}$
- $g\mu_{B}\mathbf{h} \cdot \sum_{i} \mathbf{S}_{i}^{FeA} - (1-x)g\mu_{B}\mathbf{h} \cdot \sum_{i} \mathbf{S}_{i}^{FeB} - xg\mu_{B}\mathbf{h} \cdot \sum_{i} \mathbf{S}_{i}^{GdB}$ (1)

where $\mathbf{S}_{i}^{X\alpha}$ ($\alpha = A$ -, B-sublattices and X = Fe, Gd) is the Heisenberg spin operator at *i*-site. $J_{ij}^{FeA-FeB}$, $J_{ij}^{FeB-FeB}$, $J_{ij}^{FeA-GdB}$, $J_{ij}^{FeB-GdB}$ are the exchange interaction constants between the A-B and B-B magnetic ions at the *i* and *j* sites. $D_{i}^{X\alpha}$ are the constants of the single-ion anisotropy, **h** is a magnetic field along the *z*-axis, which is also the axis of the easy magnetization, *x* is the Gd doping concentration.

The Hamiltonian of the magnetic system is built under the following assumptions:

1. The Gd³⁺-ions substitute only the Fe²⁺-ions at the octahedral sites (B-sublattice). The tetrahedral sites have a volume smaller than the octahedral ones and the radius of the Gd³⁺-ions (1.07 Å) is larger than that of the Fe²⁺-ions (0.70 Å). Thus, the structural formula of the doped magnetite with Gd ions is as follows: $[Fe_A^{3+}][Fe_{1-x}^{2+}Gd_x^{3+}Fe^{3+}]_BO_4$. This is valid for Gd concentrations up to x = 0.5. This is the concentration range in which the magnetic phase transition temperature in doped magnetite is biocompatible in the sense for medical applications. Above these concentrations, the Gd³⁺ ions replace the Fe³⁺ ions in the tetrahedral sites [13].

- 2. The magnetic interaction between the magnetic ions in the tetrahedral sites (A-O-A) is neglected because it is shown experimentally to be 10 times smaller compared to the other interactions B-O-B and A-O-B [16].
- 3. The substitution of the Fe-ion by the RE Gd³⁺-ion (B-sublattice) does not lead to a change in the interaction character of the Fe-ions between the A- and B-sublattices. This assumption is related to the fact that the antiferromagnetic nature of the interaction between octahedral and tetrahedral sites is preserved and makes possible the use of the Neel model for antiferromagnetism.

For the magnetite, a strong-spin phonon interaction has been demonstrated [18], which, from the microscopic point of view, renormalizes the magnetic exchange interactions. This is taken into account with the following Hamiltonian:

$$H_{sp} = -\frac{1}{2} \sum_{i,j,k} F(i,j,k) Q_i S_j^{X\alpha z} S_k^{X\alpha z} - \frac{1}{4} \sum_{i,j,k,l} R(i,j,k,l) Q_i Q_j S_k^{X\alpha z} S_l^{X\alpha z} + h.c.$$
(2)

where F_{ijk} and R_{ijkl} are the spin-dependent lattice vibration constants, which are the first and second derivatives of the exchange interaction constants in relation to the phonon displacements, respectively. Q_i is the normal coordinate of the lattice mode.

The spontaneous magnetization M_s of the Gd-doped Fe₃O₄ is

$$M_s = \mid M_A - M_B \mid . \tag{3}$$

 M_A and M_B are the magnetizations of the two sublattices:

$$M_A = M^{FeA}; \qquad M_B = (1 - x)M^{FeB} + xM^{GdB},$$
 (4)

where $M^{X\alpha} = (1/N) \sum_i \langle (S_i^{X\alpha})^z \rangle$ with X = Fe, Gd and $\alpha =$ A, B.

 $\langle (S_i^{X\alpha})^z \rangle$ is determined from the following expression:

$$\langle (S_i^{X\alpha})^z \rangle = \left[(S^{X\alpha} + 0.5) \operatorname{coth}[(S^{X\alpha} + 0.5)\beta E_i^{X\alpha}] - 0.5 \operatorname{coth}(0.5\beta E_i^{X\alpha}) \right],$$
(5)

where $\beta = \frac{1}{k_B T}$ and $E_i^{X\alpha} = (1/N^{\alpha}) \sum_j E_{ij}^{X\alpha}$. E_{ij} is the excitation energy observed from the poles of the following Green's functions:

$$\langle \langle S_{i}^{FeA+}; S_{j}^{FeB-} \rangle \rangle; \langle \langle S_{i}^{FeB+}; S_{j}^{FeA-} \rangle \rangle; \langle \langle S_{i}^{GdB+}; S_{j}^{FeA-} \rangle \rangle; \langle \langle S_{i}^{FeA+}; S_{j}^{GdB-} \rangle \rangle; \langle \langle S_{i}^{FeB+}; S_{j}^{FeB-} \rangle \rangle; \langle S_{i}^{FeB+}; S_{i}^{FeB-} \rangle \rangle; \langle S_{i}^{FeB+}; S_{i}^{FeB-} \rangle \rangle; \langle S_{i}^{FeB+}; S_{i}^{FeB-} \rangle \rangle; \langle \langle S_{i}^{FeB+}; S_{i}^{FeB-} \rangle \rangle; \langle S_{i}^{FeB+}; S_{i}^{FeB-} \rangle \rangle;$$

where the operators $S_i^{X\alpha_{\pm}}$ are determined from the following expression: $(S_i^{X\alpha})^{\pm} = (S_i^{X\alpha})^x \pm i(S_i^{X\alpha})^y$.

The spin-phonon interaction is observed within the mean field approximation. This leads to a renormalization of the exchange interactions in the system making them temperature dependent $J_{eff} = J + 2F^2/(\omega_0 - RM_s)$ where ω_0 is the harmonic frequency of the polar lattice mode and J is a formal denotation for all exchange interaction constants.

As mentioned in the Introduction, by doping the magnetite with RE ions, the band gap width increases. The band gap width in Fe_3O_4 defines the latter as a semiconductor, which makes these oxide NPs suitable for optical sensors. The changes in the magnetic characteristics caused by the Gd doping will cause changes in the band structure and the width of the band gap. We will account for this influence by including in the Hamiltonian of the system the interaction *I* between the localized spins and conduction ones at the *i* site, i.e., the s-d model:

$$H_{s-d} = \sum_{i} I \mathbf{S}_{i}^{X\alpha} \cdot \mathbf{s}_{i}, \tag{6}$$

where \mathbf{s}_i are the spin operators of the conduction electrons.

Then, we can define the band gap energy E_g as the difference between the valence and conduction bands:

$$E_g = \xi^+ (\mathbf{k} = 0) - \xi^- (\mathbf{k} = \mathbf{k}_\sigma)$$
(7)

with the electronic energies

$$\varepsilon_{\sigma}^{\pm}(k) = \epsilon_k - 0.5\sigma I M_s \tag{8}$$

which are observed from the Green's functions [19] $g(\mathbf{k}\sigma) = \ll c_{k\sigma}; c_{k\sigma}^+ \gg, \sigma = \pm 1$ where $c_{i\sigma}^+$ and $c_{i\sigma}$ are Fermi-creation and -annihilation operators.

3. Results and Discussion

In the numerical calculations, we will use a model of a spherical, cubooctahedral, structurally heterogeneous NP composed of core and surface shell. A nanoparticle is defined by fixing the origin at a certain Fe spin in the center of the particle and including all spins within the particle into shells numbered by n = 1, ..., N, where n = 1 is the central spin and n = N—the surface shell. In our case, the the NPs offer an icosahedral symmetry, i.e., there are 12 spherical particles in the first shell, 42 in the second shell, 92 ones in the third shell, etc.

The exchange interaction $J_{ij} \equiv J(r_i - r_j)$ depends inversely on the lattice parameters. The surface effects are included by the exchange interaction constant on the surface layer J_s , which is different from the bulk one J_b . The indices *s* and *b* are used for all model parameters.

The calculations are made for non-interacting NPs with a diameter below 80 nm. The reason is that the dipole-dipole interaction between magnetic NPs is important. It modifies their magnetic anisotropy, which will affect the magnetic characteristics of the latter. The dipole-dipole interaction itself depends on the geometrical arrangement of particles. The inclusion of this effect, in our opinion, would lead to further complication from a theoretical point of view without significantly modifying the qualitative picture of the described processes.

Since the magnetite is an inverse spinel, the super-exchange interaction between the magnetic A- and B-sublattices is antiferromagnetic. This is the most intense interaction compared to the others, so that it practically determines the magnetic structure of Fe_3O_4 . The interaction in the sublattices is ferromagnetic. As we mentioned in the introduction, the interaction between the magnetic moments in the tetrahedral sites is weakest and will be neglected. For the exchange interaction constants, we will use the following values: $J^{FeB-FeB} = 7.31$ K, $J^{FeA-FeB} = -33.9$ K, $J^{FeA-FeA} = 0$ [20]. By doping, the Gd³⁺ ions substitute the Fe²⁺ ions from the octahedral sites. If we assume that the interaction between the spins of the Gd^{3+} ions with the Fe^{3+} ions in the octahedral sites is ferromagnetic and taking into account the inequality $S(Gd^{3+}) = 7/2 > S(Fe^{2+}) = 2$, then the saturation magnetization should increase with increasing the doping concentration. However, experimental results show that for 0 < x < 0.5 the saturation magnetization decreases [13]. This is only possible if $J^{FeB-GdB}$ is antiferromagnetic, i.e., $J^{FeB-GdB} < 0$. Such an antiferromagnetic interaction has also been reported in Gd-Fe alloys [21] and, following the method of determining the exchange interaction between Gd and Fe ions in the same paper, we obtain $J^{FeB-GdB} = -2.28$ K. For the interaction between the spins of the Gd ions at the octahedral sites and the spins of the iron ions at the tetrahedral sites, we will assume that it is also antiferromagnetic, but weaker than J^{FeA-FeB} because as the ion doping increases, the magnetic phase transition temperature strongly decreases. This could be due to the weaker overlap of the 4f orbitals and the p ones of the oxygen anion acting as a mediator in the double-exchange interaction. Based on these results for the numerical value of $J^{FeA-GdB}$, we get the following: $I^{FeA-GdB} = -10.5$ K. Let us emphasize that we investigate small doping concentrations so we can neglect the interaction between the Gd ions in the octahedral sites, i.e., $J^{GdB-GdB} = 0$ K. From experimental data [18] for the spin-phonon interaction constants, we get the following: F = 27.3 K and R = -23.5 K. For the single ion anisotropy constant D, we use for the bulk compound D^{Fe} (bulk) = -0.87 K [22]; whereas for single

domain NPs for the surface anisotropy, we use D^{Fe} (surface) = -0.28 K [23]. RE ions have a large value of single-ion magnetic anisotropy; therefore, we will assume a value of one order of magnitude larger compared to that of the iron ions D^{Gd} = 8.7 K. By the numerical calculations of the NPs we will consider a core with microscopic parameters such as bulk material. The shell has changed parameters due to the interrupted translational invariance, uncompensated bonds and oxidation. With the index "s", we will denote the interactions on the surface while with "b" in the volume. As for the decrease of the NP size in the pure magnetite, a reduction of the phase transition temperature is observed. We believe that the following relation between the surface and bulk exchange interaction constants hold true for all exchange interactions: $J_s < J_b$.

The NP is composed of shells, with each subsequent shell containing an increasing number of atoms. The model is constructed from cubooctahedra or truncated octahedra with a tightly packed cubic crystal structure [24]. The first built shell is composed of equilateral triangles. In the subsequent shells, cubooctahedrons appear, which are surrounded by triangular and square walls. The NP is defined fixing the origin in an arbitrary spin at the centre of the particle and arranging all the remaining spins in the particle on shells [25]. The shells are denoted by n = 0.1, ..., N, where n = 0 denotes the central spin and n = N represents the surface shell of the NP.

3.1. Size Dependence of the Magnetization and Curie Temperature

At first, we will present numerical calculations of the dependence of the spontaneous magnetization M_s and the magnetic phase transition temperature T_C on the size of Fe₃O₄ NPs. Let us emphasize that the lattice parameters of the NPs increases slightly compared to the bulk value [26].

The results are presented in Figures 1 and 2. With a decrease of the size of the NP, M_s and T_C decrease. A similar decrease of M_s in Fe₃O₄ NPs is observed experimentally by Mohapatra et al. [27]. Let us emphasize that M_s decreases with increasing temperature and vanishes at T_C . Moreover, M_s and T_C depend on the spin value *S* and the exchange interaction constants J_s and J_b . A similar effect, a decrease with decreasing *d*, is observed also for the Curie temperature T_C (see Figure 2). We obtain $T_C \approx 690$ K for d = 20 nm and $T_C \approx 600$ K for d = 10 nm. The decrease is due to size and surface effects becoming predominant as the ratio surface to core volume increases. Below d = 10 nm, we have a superparamagnetism. It must be mentioned that Mohapatra et al. [27] obtained a T_C value of 665 K for d = 10 nm for Fe₃O₄ NPs, whereas Manohar et al. [28] reported $T_C = 713$ K for d = 12 nm. Using Monte Carlo simulation, Maazouzi et al. [20] calculated for thin magnetite films a T_C increase with increasing film thickness.



Figure 1. Size dependence of the spontaneous magnetization M_s of a pure Fe₃O₄ NP, $J_s = 0.9 J_b$.



Figure 2. Size dependence of the Curie temperature T_C for a pure Fe₃O₄ NP, $J_s = 0.9J_b$.

Qualitatively, these results can be explained as follows: with decreasing the NP size, the surface area/volume ratio increases, i.e., the influence of the surface on the structural and magnetic characteristics increases. The oxidation, broken bonds at the surface, unpaired electron orbitals, and increased surface anharmonism lead to reduction of the net magnetic moment. Therefore, as the influence of the surface grows (i.e., the diameter of the magnetic NP decreases), the total magnetization become smaller. The decrease of the phase transition temperature with size reduction of the NP can be qualitatively explained by the fact that, with decreasing the size, the volume of the elementary cell increases, which leads to an increase in the distance between the spins. To the extent that the exchange interaction is highly sensitive to the distance between the interacting magnetic ions, this will lead to a decrease of the exchange interaction in the shell and at the surface of the magnetic NP and to a reduction of T_C . The observed qualitative coincidence with the experimental results is evidence that the presented microscopic model of magnetic NPs adequately represents and explains the main magnetic characteristics of Fe₃O₄ NP and their dependence on surface and size effects.

3.2. Gd Doping Dependence of the Magnetization and Curie Temperature

Next, we will study the influence of RE ion doping on the spontaneous magnetization M_s and the Curie temperature T_C . It must be mentioned that the Gd ions substitute the Fe ions in the whole NP, in the surface shell and in the bulk, in the core. Moreover, due to the different ionic radii of the Gd and the Fe ions, there appear a strain which changes the interaction constants at the doped state noted as J_d compared to the undoped one J_b . The results for Gd doping for $0 \le x \le 0.2$ on the spontaneous magnetization M_s and the Curie temperature T_C are shown in Figures 3 and 4, respectively. It is clearly seen that the Gd ion doping leads to decrease of M_s and T_C . Zhang et al. [14] reported also a slightly decreased magnetization at 260 K in Gd-doped Fe₃O₄ NPs in contrast to the undoped ones. A similar decrease of M_s is observed also in Ce [29] or Dy, Nd, La doped Fe₃O₄ NPs [12]. We observe for Gd-doped Fe₃O₄ NPs a T_C value of 312 K for x = 0.2. Thorat et al. [30] and Sun et al. [31] have obtained also a decrease of the critical temperature T_C of Gd-doped Fe₃O₄ NPs. Moreover, a decrease of the magnetic coercive field, the remanent magnetization and the Curie temperature with decreasing the thickness of a Fe₃O₄ thin film is reported recently by Maazouzi et al. [20].

The decrease of the magnetization and magnetic phase transition temperature with doping qualitatively is explained as follows: The larger ionic radius of Gd^{3+} compared to the Fe²⁺ radius leads to an increase in the volume of the elementary cell. As a consequence, the distance between the interacting magnetic moments increases, which leads to a decrease in the exchange interaction constants and to a decrease of T_C . Although the net magnetic moment of the Gd ion $(7\mu_B)$ is larger compared with that of the Fe²⁺ ion $(5\mu_B)$, M_s and the saturation magnetization decrease. This is a consequence of the antiferromagnetic arrangement of the Gd and Fe spins at the octahedral sites. The interaction between the

magnetic moments of the RE and the Fe³⁺ ions in the tetrahedral sites is antiferromagnetic, which means that, in the A sublattice, antiparallel iron spins will appear, leading to an additional reduction of M_s and the saturation magnetization. Speculation suggests that competing magnetic interactions arise due to Gd doping, leading to magnetic system frustration and the potential emergence of non-collinear structures. However, there is a lack of experimental results either confirming or refuting this hypothesis.



Figure 3. Gd doping concentration dependence of the spontaneous magnetization M_s of a Fe₃O₄ NP, d = 20 nm, $J_d = 0.8J_b$.



Figure 4. Gd doping concentration dependence of the Curie temperature T_C of a Fe₃O₄ NP, d = 20 nm, $J_d = 0.8J_b$.

Let us emphasize that Daoush [9] have studied Co-doped Fe₃O₄ NPs with $d \approx 30$ nm and reported a decrease of M_s and T_c . This result can be confirmed from our model. The ionic radius of Co is larger compared to that of the Fe ion, i.e., the tensile strain that appears leads to a decrease of the magnetization and the Curie temperature. The transition metal ion-doped Fe₃O₄ NPs will be investigated in a future paper.

3.3. Size and Gd Doping Effects on the Band Gap

Finally, we studied the band gap energy E_g of Fe₃O₄ NPs as a function of size and ion doping. Radon et al. [32] reported that, with decrease in the crystallite size, the optical band gap energy E_g increases. The result for the band gap width E_g of Gd-doped Fe₃O₄ NPs is presented in Figure 5. We find a blue shift for E_g with increasing the doping with RE ions. The direct optical band gap E_g of pure Fe₃O₄ NPs is around 2.2 eV [12], which may vary with particle size, composition and structure. We observe that E_g for a pure Fe₃O₄ NP is slightly larger than that of a bulk one (2.0 eV [12]), which is related to surface effects (not shown here).



Figure 5. Gd doping concentration dependence of the band gap energy E_g of a Fe₃O₄ NP for $J_d = 0.8J_b$.

The band gap energy E_g is enhanced with increasing Gd dopants due to the tensile strain which appears by the ion doping. As we discussed in Section 3.1, the growth of the crystal lattice volume and the appearance of an antiferromagnetic ordering between the spins of Gd and Fe in the octahedral sites reduces the spontaneous magnetization M_s for small doping concentration x (see Figure 3). Then, it is clear from Equation (8) that, with increasing x, the band width E_g increases.

Our model could explain also the enhanced band gap energy by doping with other RE ions, as experimentally found by Kershi et al. [12] for Dy, Nd, La doped Fe_3O_4 NPs. The RE ions have, similar to that of the Gd ion, an ionic radius larger than that of the Fe ion, but they have no biological role.

4. Conclusions

Based on a microscopic model and the method of the Green's functions, this article presents analytical and numerical calculations of the magnetic and optical properties of a pure and Gd^{3+} -doped magnetite NP with the chemical formula Fe₃O₄. The investigations were carried out under the assumptions that the sample of $[Fe_A^{3+}][Fe_{1-x}^{2+}Gd_x^{3+}Fe^{3+}]_BO_4$ NP is monodisperse and there is not interaction between the NPs.

The magnetization M_s and the Curie temperature T_C are calculated depending on size, temperature, and Gd doping concentration. In qualitative agreement with the experimental data, we observe that M_s and T_C decrease with decreasing NP size and with increasing Gd doping concentration. The band gap energy E_g increases with decreasing NP size and Gd dopants.

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