Theoretical investigation on the magnetization enhancement of Fe$_3$O$_4$-reduced graphene oxide nanoparticle system

M A Majidi$^1$, Y Wicaksono$^1$, A D Fauzi$^1$, A Taufik$^1$, R Saleh$^1$ and A Rusydi$^{2,3}$

$^1$Department of Physics, Faculty of Mathematics and Natural Sciences Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia
$^2$NUSNNI-NanoCore, Department of Physics, Faculty of Science, National University of Singapore, Singapore 117576, Singapore
$^3$Singapore Synchrotron Light Source, National University of Singapore, Singapore 117603, Singapore

Corresponding author’s email: aziz.majidi@sci.ui.ac.id

Abstract. We present a theoretical study on the enhancement of magnetization of Fe$_3$O$_4$ nanoparticle system upon addition of reduced graphene oxide (rGO). Experimental data have shown that the magnetization of Fe$_3$O$_4$-rGO nanoparticle system increases with increasing rGO content up to about 5 wt%, but decreases back as the rGO content increases further. We propose that the enhancement is due to spin-flipping of Fe ions at the tetrahedral sites assisted by oxygen vacancies at the Fe$_3$O$_4$ particle boundaries. These oxygen vacancies are induced by the presence of rGO flakes that adsorb oxygen atoms from Fe$_3$O$_4$ particles around them. To understand the enhancement of the magnetization, we construct a tight-binding based model Hamiltonian for the Fe$_3$O$_4$ nanoparticle system with the concentration of oxygen vacancies being controlled by the rGO content. We calculate the magnetization as a function of the applied magnetic field for various values of rGO wt%. We use the method of dynamical mean-field theory and perform the calculations for a room temperature. Our result for rGO wt% dependence of the saturated magnetization shows a very good agreement with the existing experimental data of the Fe$_3$O$_4$-rGO nanoparticle system. This result may confirm that our model already carries the most essential idea needed to explain the above phenomenon of magnetization enhancement.

1. Introduction

Fe$_3$O$_4$, informally known as magnetite, is a magnetic material with ferrimagnetic ordering. Due to its half-metallic characteristic with 100% spin polarization at the Fermi level [1, 2] and high Curie temperature ($\sim 851$ K), magnetite becomes a prospective material for spintronic devices [3–5]. To some extent, Fe$_3$O$_4$ nanoparticles still preserve the magnetic properties as those of bulk Fe$_3$O$_4$. Due to high Curie temperature and biocompatibility [6], Fe$_3$O$_4$ nanoparticle system also becomes promising for use in photo-catalysis and biomedical applications [7, 8].

A recent study by Taufik et al. suggests that the magnetization of Fe$_3$O$_4$ nanoparticle system enhances when mixed with reduced graphene oxide (rGO) [9]. The mechanism behind this magnetization enhancement has still not been fully understood. However, a hint to explanation of this phenomenon may be given by another recent experimental study by Herng et al., suggesting that the magnetization enhancement occurs due to spin flipping of Fe ions at tetrahedrally coordinated sites, which is suspected...
Figure 1. The system of Fe$_3$O$_4$ nanoparticle clusters (a) without additional rGO, (b) with additional rGO less than 5 wt%, (c) with additional rGO of $\sim$ 5 wt% and (d) with additional rGO more than 5 wt%

to be induced by oxygen vacancies. These spin flippings lead the system to transform from ferrimagnetic to ferromagnetic ordering [10]. Motivated by that experimental hint, we develop the idea and propose a theoretical study to explain the magnetization enhancement phenomenon of the Fe$_3$O$_4$-rGO nanoparticle system. We hypothesize that the magnetization enhancement of Fe$_3$O$_4$-rGO nanoparticle system is induced by oxygen vacancies formed on the surface of Fe$_3$O$_4$ nanoparticle clusters due to the presence of rGO flakes nearby the Fe$_3$O$_4$ clusters. This argument is based on a previous experimental study by Santoso et al. [11], supported by a theoretical study by Majidi et al. [12], indicating that graphene can easily adsorb oxygens. Our main goal is to calculate magnetization of Fe$_3$O$_4$ nanoparticle system with and without oxygen vacancies, and use this to mimic the experimental data of magnetization of the combined Fe$_3$O$_4$-rGO nanoparticle system by connecting the concentration of oxygen vacancies with the rGO content.

2. Model of Fe$_3$O$_4$-rGO nanoparticle system

The experimental data of reference [9] shows that the magnetization of Fe$_3$O$_4$-rGO nanoparticle system increases with increasing rGO content up to about 5 wt%, but decreases back as the rGO content increases further. We propose a model to explain this situation as illustrated in figure 1. When there is no rGO content (figure 1(a)), all the Fe$_3$O$_4$ clusters are assumed to have no oxygen vacancies. As the system is added with rGO content less than 5 wt% (figure 1(b)), rGO flakes start to fill spaces in between neighboring Fe$_3$O$_4$ clusters. At this low concentration of rGO, we suppose that each space between two neighboring Fe$_3$O$_4$ clusters can only be filled by at maximum of one layer of rGO flake. The insertion of an rGO flake induces the extraction of oxygen atoms from the nearby Fe$_3$O$_4$ clusters, which then get adsorbed onto the rGO surface. As a result, oxygen vacancies are formed on the surfaces of Fe$_3$O$_4$ clusters, inducing spin flippings of the Fe ions at tetrahedral sites in those clusters, thus increasing the total magnetization of the whole system by some amount. We suppose that when the rGO content is $\sim$ 5 wt% (figure 1(c)), each space between neighboring Fe$_3$O$_4$ clusters has been filled with one rGO layer. At this rGO concentration, the adsorption of oxygen atoms by the rGO flakes is optimum, hence the enhancement of magnetization of the system becomes maximum. When the rGO content is exceeding 5 wt% (figure 1(d)), there are some spaces between Fe$_3$O$_4$ clusters that are filled with rGO flakes of more than one layer. The increase of number of layers of an rGO flake does not increase its capability of adsorbing oxygen atoms since the area of its open surfaces remains the same. However, the addition of more rGO content without more formation of oxygen vacancies in Fe$_3$O$_4$ clusters causes the total magnetization per unit mass of the system to decrease. Therefore, adding rGO flakes of more than 5 wt% decreases the total magnetization per unit mass of the system monotonically.

The rGO content added to Fe$_3$O$_4$ nanoparticles is experimentally measured using weight percent unit (wt%). This weight percentage can be understood as ratio of the total mass of rGO flakes to the total
mass of Fe$_3$O$_4$ clusters. Mathematically, we can formulate it as follows

$$x = \frac{N_G M_G}{N_F M_F},$$  \hspace{1cm} (1)$$

where $N_F$ and $N_G$, respectively, are the number of Fe$_3$O$_4$ clusters and rGO layers in the system, $M_F$ and $M_G$ are the averaged mass of Fe$_3$O$_4$ clusters and the averaged mass of rGO layers, respectively, while $x$ is wt% of rGO layers added to the Fe$_3$O$_4$ nanoparticles.

Now, let the mass ratio of Fe$_3$O$_4$ clusters to rGO flakes be $\alpha$. As an Fe$_3$O$_4$ cluster is likely heavier than an rGO layer, $\alpha$ should be larger than unity. In our model, a space between neighboring Fe$_3$O$_4$ clusters can be filled by an rGO flake or one or more layers. How rGO layers fill such spaces affects the magnetization enhancement of the system. Hence, we include this into our model. Let $n$ be the maximum number of rGO layers filling a space between two Fe$_3$O$_4$ clusters while the system still allows a vacant space. This means, no space will get filled with an rGO flake of more than $n$ layers as long as there is still a vacant space. Hence, ratio of the total number of rGO layers in the system to the maximum number of rGO layers that can be accommodated by the system with no vacant spaces can be formulated as

$$\beta = \frac{N_G}{N_G \text{max}} = \frac{N_G}{n N_F} = \frac{x \alpha}{n}.$$  \hspace{1cm} (2)$$

Based on the definition of $n$ stated above, the probability of finding a space between two Fe$_3$O$_4$ clusters with no rGO flake is

$$P_0 = \begin{cases} (1 - \beta)^n, & \text{if } \beta < 1 \\ 0, & \text{if } \beta \geq 1, \end{cases}$$  \hspace{1cm} (3)$$

while the probability of finding an rGO flake containing one or more layers between two Fe$_3$O$_4$ clusters is $1 - P_0$. When rGO flakes are added to the Fe$_3$O$_4$ nanoparticles with random distribution, we expect that the resulting net magnetization of the system is contributed by the magnetic moments of the unit cells inside of Fe$_3$O$_4$ clusters that have no oxygen vacancies and those on the surfaces of the Fe$_3$O$_4$ clusters some of which have oxygen vacancies. For simplicity, let us assume that each Fe$_3$O$_4$ cluster has the same number of unit cells making up the total mass of $M_F$ for each cluster. Likewise, let us assume each rGO layer contains the same number of graphene unit cells making up the total mass of $M_G$ for each layer. Further, let $\mu_0$ be the magnetic moment of an Fe$_3$O$_4$ cluster with no oxygen vacancies, and $\mu_v$ be the magnetic moment of an Fe$_3$O$_4$ cluster assuming all the Fe$_3$O$_4$ unit cells in it has an oxygen vacancy. Lastly, let $\gamma$ be the portion of unit cells in an Fe$_3$O$_4$ cluster that have oxygen vacancies. Thus, we may construct the relation between the total magnetization $\mathcal{M}$, that depends on the rGO content $x$, with the quantities just described as

$$\mathcal{M}(x) = \frac{P_0 N_F \mu_0 + (1 - P_0) N_F \gamma \mu_v}{N_F M_F + N_G M_G},$$  \hspace{1cm} (4)$$

with $\mathcal{M}_0 = \frac{\mu_0}{\gamma}$. By dividing both the numerator and the denominator with $N_F M_F$, the equation can be rearranged to be

$$\mathcal{M}(x) = \frac{P_0 \mathcal{M}_0 + (1 - P_0) \gamma \mathcal{M}_v}{1 + n \frac{\beta}{\alpha}}.$$  \hspace{1cm} (5)$$

To use equation (5), we first specify the $n$ value corresponding to the model we choose. Next, for every $x$ value we take $\beta$ according to equation (2), and then $P_0$ according to equation (3). Along with $n$, $\gamma$ and $\alpha$ can be adjusted to obtain the best fit to the experimental data. As for $\mathcal{M}_0$, we take the empirical value of the saturation magnetization from the experimental data, that is $\sim 80$ emu/g. Whereas, $\mathcal{M}_v$ is the theoretical value of the saturation magnetization if spin flipping occurs in all unit cells in the
cluster induced by oxygen vacancies, that is \( M' = 3M_0 \). The expected realistic value of the saturation magnetization in an Fe\(_3\)O\(_4\) cluster if spin flipping occurs in some portion, \( \gamma \), of all unit cells on the surface of the cluster, would be \( \gamma \cdot M' \).

3. Model to calculate the magnetization as a function of temperature and external magnetic field

To calculate the magnetization of the system as a function of temperature and external magnetic field, we model the Fe\(_3\)O\(_4\) nanoparticle cluster as if it is a bulk system. The model has been proposed in our recent study [13]. Following reference [13], we use (001) Fe\(_3\)O\(_4\) surface and simplify the crystal structure by taking only the bottom-most two-layers of the actual unit cell. The half metallic property along the (001) Fe\(_3\)O\(_4\) surface has been confirmed by first-principle calculation [14]. We further simplify the unit cell by restricting only the square block containing one unit of Fe\(_3\)O\(_4\) as shown in figure 2. With this model unit cell, for the system without oxygen vacancies (referring to figure 2(a)), we choose 11 basis atomic orbitals to construct our Hilbert space, that we order as follows: \( |O_{A} - p_{\uparrow}\rangle, |O_{A} - p_{\downarrow}\rangle, |O_{B} - p_{\downarrow}\rangle, \), \( |O_{C} - p_{\downarrow}\rangle, |O_{C} - p_{\uparrow}\rangle, |O_{D} - p_{\downarrow}\rangle, |O_{D} - p_{\uparrow}\rangle, |FeA - e_{\uparrow}\rangle, |FeA - e_{\downarrow}\rangle, |FeB_{1} - e_{\uparrow}\rangle \) and \( |FeB_{2} - e_{\uparrow}\rangle \). The 11 basis orbitals along with the two spin orientations make up a set of 22 basis states. Whereas, for the system with oxygen vacancies, we remove one oxygen atom, i.e. \( O_{B} \), hence removing also \( |O_{B} - p_{\uparrow}\rangle \) and \( |O_{B} - p_{\downarrow}\rangle \) orbitals, leaving only 9 basis orbitals or 18 basis states remaining. Using the above sets of basis states, we propose our model Hamiltonian as

\[
H = \sum_{k} [a_{k}]^{\dagger} [H_{0}(k)] [a_{k}] - J_{H} \sum_{i} S_{i} S_{i} + U \sum_{i} n_{\uparrow,i} n_{\downarrow,i}. \tag{6}
\]

The first term in the Hamiltonian is the kinetic term which is constructed using tight-binding approximation. Here, \([a_{k}]\) is a column vector containing the corresponding fermion annihilation operators, while \([a_{k}]^{\dagger}\) is its hermitian conjugate, with \( k \) index denotes the \( k \)-points in the Brillouin zone. \( [H_{0}(k)] \) is a 22 \times 22 (18 \times 18) matrix in momentum space for the system without (with) oxygen vacancies, constructed using tight-binding approximation, which consists of four 11 \times 11 (9 \times 9) blocks corresponding to their spin directions as

\[
[H_{0}(k)] = \begin{bmatrix} H_{0}(k)_{\uparrow} & 0 \\ 0 & H_{0}(k)_{\downarrow} \end{bmatrix}. \tag{7}
\]

See reference [13] for the detailed content of \( [H_{0}(k)] \) for both systems without and with oxygen vacancies. The second term represents the magnetic exchange interaction between the collective spin
S of the $t_{2g}$ electrons and the spin s of an $e_g$ electron in each Fe ion, with $i$ denoting the site of the Fe ion, and $J_H$ being Hund’s coupling constant. The last term represents the Coulomb repulsive interaction between two electrons occupying the same Fe-$e_g$ orbital, with $n_{i\sigma}$ being the electron occupation number operator at site $i$ with spin component $\sigma$, and $U$ the Hubbard parameter. To simplify our calculations, we replaced this term with the mean-field approximated version, that is

$$U \sum_i n_{i\uparrow} n_{i\downarrow} = U \sum_i \langle n_{i\uparrow} \rangle n_{i\downarrow} + \langle n_{i\downarrow} \rangle n_{i\uparrow} - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle,$$

with $\langle n_{i\sigma} \rangle$ to be calculated self-consistently.

4. Calculation Methods

We use dynamical mean-field theory (DMFT) algorithm to calculate magnetization of the system. We begin the algorithm by defining the Green function matrix for our system as

$$[G(k, z)] = \left[ zI - [H_0(k)] - [\Sigma(z)] \right]^{-1},$$

where $z$ is the complex frequency variable defined as $z = \omega + i0^+$ for the real-frequency domain and $z = i\omega_n + \mu$ for the Matsubara-frequency domain, with $\omega_n = (2n + 1)\pi T$ being fermion Matsubara frequency, $T$ temperature and $\mu$ chemical potential. Note that throughout this paper, we set $\hbar = k_B = 1$. Here, the self-energy matrix $[\Sigma(z)]$, along with $\langle n_{i\sigma} \rangle$, are taken from initial guess. We then average the Green function matrix over all $k$-points in the Brillouin zone as

$$[G(z)] = \frac{1}{N} \sum_k [G(k, z)],$$

where $N$ is the number of $k$-points in the Brillouin zone. Next, we extract the mean-field Green function matrix through

$$[G(z)]_{MF} = \left[ [G(z)]^{-1} + [\Sigma(z)] \right].$$

We use this mean-field Green function matrix to calculate the local interacting Green function matrix that depends on the orientation of the three Fe spins

$$[G(z, \theta_1, \theta_2, \theta_3)]_{loc} = \left[ [G(z)]_{MF}^{-1} - [\Sigma(\theta_1, \theta_2, \theta_3)]_{loc} \right]^{-1},$$

where $[\Sigma(\theta_1, \theta_2, \theta_3)]_{loc}$ is the local self-energy matrix manifesting the dynamics of the Coulomb repulsive interactions and magnetic exchange interactions at a local unit cell, containing the dependence on the angles $\theta_1, \theta_2$ and $\theta_3$, of the three Fe spins with respect to the direction of net magnetization (taken as the direction of the positive $z$ axis), and the averaged occupancies of electrons at Fe-$e_g$ orbitals, $\langle n_{i\sigma} \rangle$. The detailed form of $[\Sigma(\theta_1, \theta_2, \theta_3)]_{loc}$ can be seen in reference [13].

Now $[G(z, \theta_1, \theta_2, \theta_3)]_{loc}$ must be averaged over all possible orientations of the three Fe spins in a unit cell. The averaging process is implemented using the Boltzmann weight defined as

$$P(\theta_1, \theta_2, \theta_3) = \frac{1}{Z} e^{-S_{eff} + \hbar S(\cos \theta_1 + \cos \theta_2 + \cos \theta_3)/T},$$

where

$$S_{eff} = -\sum_n \ln \det \left[ [G_{MF}(i\omega_n)] [G_{loc}^{-1}(i\omega_n, \theta_1, \theta_2, \theta_3)] \right] e^{i\omega_n 0^+},$$

is the effective action, which is calculated only in Matsubara-frequency domain and
of each function. The calculated chemical potential is then used to update the averaged electron occupancy through

\[
Z = \int \int d\theta_1 d\theta_2 d\theta_3 e^{-S_{\text{MF}} + hS(\cos \theta_1 + \cos \theta_2 + \cos \theta_3)/T},
\]

(15)

serves as the partition function. The term \( hS(\cos \theta_1 + \cos \theta_2 + \cos \theta_3)/T \) is added to accommodate the effect of external magnetic field \( h \) (defined in unit of energy) at a temperature \( T \). Thus, the averaged interacting Green function matrix is obtained through

\[
G_{\text{ave}}(z) = \int \int d\theta_1 d\theta_2 d\theta_3 \left[ G_{\text{loc}}(z, \theta_1, \theta_2, \theta_3) \right] P(\theta_1, \theta_2, \theta_3).
\]

(16)

This averaging process is also used to calculate the magnetization through

\[
M = \int \int P(\theta_1, \theta_2, \theta_3) S(\cos \theta_1 + \cos \theta_2 + \cos \theta_3) d\theta_1 d\theta_2 d\theta_3.
\]

(17)

The new self-energy matrix can then be extracted as

\[
[\Sigma(z)] = [G_{\text{MF}}(z)]^{-1} - [G_{\text{ave}}(z)]^{-1}.
\]

(18)

Along with the self-energy matrix, we also need to update the chemical potential, \( \mu \), by imposing a fixed electron filling per unit cell, that is \( n_{\text{filling}} = 20 \) for the system without oxygen vanancies, such that

\[
n_{\text{filling}} = \int d\omega \text{DOS}(\omega) f(\omega, \mu, T),
\]

(19)

where

\[
\text{DOS}(\omega) = -\frac{1}{\pi} \text{ImTr}[G_{\text{ave}}(\omega + i0^+)],
\]

(20)

is the electron density of states, and \( f(\mu, \omega, T) = (e^{(\omega-\mu)/T} + 1)^{-1} \) is the Fermi-Dirac distribution function. The calculated chemical potential is then used to update the averaged electron occupancy of each \( e_g \) orbital of Fe ion at site \( i \) in a unit cell with spin component \( \sigma \) through

\[
\langle n_{i\sigma} \rangle = \int d\omega \text{PDOS}_{i\sigma}(\omega) f(\omega, \mu, T),
\]

(21)

with \( \text{PDOS}_{i\sigma}(\omega) = -(1/\pi) \text{Im} G_{\text{ave}}(\omega + i0^+) \) being the corresponding projected density of states. Finally, we iterate the algorithm using the updated self energy matrix, chemical potential and averaged electron occupancy, and the self-consistency process is repeated until convergence is achieved.

5. Results and discussion

Since in this paper we use DMFT to obtain mainly the magnetization as a function of temperature and magnetic field, we restrict our calculations only for the system with oxygen vacancies. While, for the system with oxygen vacancies, we take for granted the result of reference [13] from which the system with oxygen vacancies has a ferromagnetic ordering with magnetization being three times greater than that of the system without oxygen vacancies that has a ferrimagnetic ordering. Further, we normalize the magnetization such that the saturation magnetization of the pure FeO nanoparticle system is \( \sim 80 \) emu/g, as obtained from the experiment. For our calculations we use the following parameters: \( \varepsilon_{O\lambda} = \varepsilon_{O\alpha} = -1.5 \) eV, \( \varepsilon_{O\beta} = \varepsilon_{O\sigma} = 1.8 \) eV, \( \varepsilon_{FeA} = 0.5 \) eV, \( \varepsilon_{FeB1} = \varepsilon_{FeB2} = 0.4 \) eV, \( \varepsilon_{O_{\text{near}}} = 0.4 \) eV, \( \varepsilon_{O_{\text{far}}} = 0.3 \) eV, \( \varepsilon_{FeA-O} = 1.8 \) eV, \( \varepsilon_{FeB1-O} = 0.9 \) eV, \( \varepsilon_{FeB2-O} = 0.9 \) eV, \( \varepsilon_{FeB1-FeB2} = 0.825 \) eV, \( \varepsilon_{FeA-FeB1} = \varepsilon_{FeA-FeB2} = 1.8 \) eV, \( J_{\text{eff}} = 1 \) eV, \( U = 4 \) eV and \( n_{\text{filling}} = 20 \) electrons per unit cell.

Figure 3 shows our result of spin-resolved density of states (DOS) for a room temperature (\( \sim 300 \) K). The density of states shows that our model reveals its half-metallic characteristic, where in the majority spin channel, the chemical potential (or the Fermi level) lies inside of the band, while in the minority spin channel, the chemical potential lies outside the band. This result demonstrates that our model captures
Figure 3. Density of states (DOS) of our Fe$_3$O$_4$ model at a room temperature showing the half metallic characteristic.

Figure 4. Saturation magnetization of Fe$_3$O$_4$-rGO nanoparticle system with rGO wt% variation, for $\alpha = 20$ and $\gamma = 0.574$.

one of the most relevant characteristics of Fe$_3$O$_4$ as observed in experiment [2]. Having this result, we argue that our model is adequate to be used for further calculations.

In calculating the saturation magnetization as a function of rGO wt% ($x$), we tune the parameters $\alpha$, $\gamma$ and $n$, and find that the best fit to experimental data is obtained using $\alpha = 20$, $\gamma = 0.574$ and $n = 1$. Figure 4 shows our results of the saturation magnetization for $n = 1, 2,$ and $3$, as compared to the experimental data. By varying $n$, we can track how the distribution of number of layers of the rGO flakes influences the result. For $n = 1$, the result shows the linear increase of the saturation magnetization with increasing $x$ up to 5 wt%, after which the additional rGO flakes make the saturation magnetization decreases also almost linearly. A little discrepancy is shown by our $n = 1$ result, that is, the saturation magnetization values above $x = 5\%$ are obtained to be slightly higher than the experimental data. For higher values of $n$, the maximum saturation magnetization shifts to the right. That is because there is still a probability of finding spaces unoccupied by rGO flakes when some other spaces are already filled by rGO flakes with two (for $n = 2$) or three (for $n = 3$) layers. This mechanism also implies that the peak of saturation magnetization for $n = 2$ and $n = 3$ become broader. Meanwhile, the fact that our saturation magnetization calculation result is in agreement with experimental data for $\gamma = 0.574$ indicates that not all Fe$_3$O$_4$ unit cells have oxygen vacancies. This is because the capability of the rGO flakes to adsorb more oxygens from the Fe$_3$O$_4$ clusters are limited by the oxygen adatoms that are already precedingly attached on the graphene surface. As for the value of $\alpha$ which is about 20, it shows us that the Fe$_3$O$_4$ nanoparticle cluster is much heavier than the rGO layer which is consistent with our presumption.

The results of applied magnetic field dependent magnetization for all rGO wt% variation are shown in figure 5. The magnetization of the model for Fe$_3$O$_4$ nanoparticle system with no additional rGO flakes is represented by the black curve. While, the red curve represents the magnetization of the system with the optimum rGO content ($x = 5\%$), leading to highest saturation magnetization. For the other rGO wt% values ($x = 0.10, 0.15$ and $0.20$) the calculations are performed using equation 5. The overall trend shows by our calculation results is in agreement with the experimental data, in which the highest magnetization occurs at 5 wt% of rGO, and the magnetization subsequently decreases until the content of rGO flakes achieving 20 wt%, which is still higher than that of the pure Fe$_3$O$_4$ nanoparticle system.

In contrast to the saturation magnetization results, our calculated remanent magnetization values do not really fit with the experimental data, instead they are significantly higher than experimental data, and are rather closer to the saturation magnetization values. This is related to the fact that the Curie temperature ($T_C$) for our model of Fe$_3$O$_4$ without oxygen vacancies shown in figure 6 is much higher than
Figure 5. Magnetization as a function of applied magnetic field of our model for Fe$_3$O$_4$-rGO nanoparticle system with rGO wt% variation. Inset shows the experimental data for comparison.

Figure 6. Averaged total spin per unit cell as a function of temperature of our model for pure Fe$_3$O$_4$ without oxygen vacancies. The over-estimated $T_C$ may be attributed to the over-simplification of the model unit cell.

the experimental value of 858 Kelvin. This may partly arise as a consequent of the over-simplification of our model unit cell. Another possible source of discrepancy may come from the mean-field treatment of the Hubbard term in our model Hamiltonian, which commonly overestimates physical quantities such as $T_C$. Nevertheless, overall, our model is able to qualitatively confirm the magnetization enhancement of Fe$_3$O$_4$ nanoparticle system with addition of rGO flakes.

6. Conclusions
In conclusion, our present study supports our previous hypothesis that the enhancement of magnetization of Fe$_3$O$_4$ nanoparticle system upon addition of reduced graphene oxide (rGO) is due to spin-flipping of the Fe ions in the tetrahedral sites and that oxygen vacancies at the Fe$_3$O$_4$ nanoparticle clusters assist the occurrence of spin-flipping. The presence of rGO flakes nearby Fe$_3$O$_4$ clusters induces the formation of oxygen vacancies in the Fe$_3$O$_4$ clusters, leading to the occurrence of spin-flipping and thus enhancing the magnetization of the system. Our model for Fe$_3$O$_4$ nanoparticle cluster can describe the saturation magnetization enhancement of Fe$_3$O$_4$ nanoparticle system upon addition of reduced graphene oxide (rGO). However, our calculation method overestimates the Curie temperature and the remanent magnetization of the Fe$_3$O$_4$ nanoparticle system. This may be caused by the over-simplification of our model unit cell and the mean-field approximation used in our method.

Acknowledgements
We acknowledge and thank Universitas Indonesia, Indonesia, for the full funding provided for the completion of this project through PITTA Research Grant No. 2022/UN2.R12/HKP.05.00/2016.

References
[1] Yanase A and Siratori K 1984 J. Phys. Soc. Jpn. 53 312-7
[2] Zhang Z and Satpathy S 1991 Phys. Rev. B 44 13319-31
[3] Matsuda H, Takeuchi M, Adachi H, Hiramoto M, Matsukawa N, Odagawa A, Setsune K and Sakakima H 2002 Jpn. J. Appl. Phys. 41 L387-90
[4] Hu G and Suzuki Y 2002 Phys. Rev. Lett. 89 276601
[5] Seneor P, Fert A, Maurice J-L, Montaigne F, Petroff F and Vaurs A 1999 Appl. Phys. Lett. 74 4017
[6] Wang J, Wu W, Zhao F and Zhao G 2011 Appl. Phys. Lett. 98 083107
[7] Shariati S, Faraji M, Yamini Y and Rajabi A A 2011 Desalination 270 1605
[8] Laurent S, Forge D, Port M, Roch A, Robic C, Vander Elst L and Muller R N 2008 Chem. Rev. 108 2064-110
[9] Taufik A and Saleh R 2016 AIP Conf. Proc. 1725 020089
[10] Herng T S et al. 2015 Nano Res. 8 2935-45
[11] Santoso I, Singh R S, Gogoi P K, Asmara T C, Wei D, Chen W, Wee A T S, Pereira V M and Rusydi A 2014 Phys. Rev. B. 89 075134
[12] Majidi M A, Siregar S and Rusydi A 2014 Phys. Rev. B. 90 195442
[13] Fauzi A D, Majidi M A and Rusydi A 2017 J. Phys.: Condens. Matter 29 135802
[14] Cheng C 2005 Phys. Rev. B 71 052401