The magnetic properties of Fe$_3$O$_4$ thick films as described by third order perturbed Heisenberg Hamiltonian

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Received: 23/01/2019; Accepted: 30/05/2019

Abstract: Thick films of Fe$_3$O$_4$ up to 10000 spin layers have been explained using third order perturbed modified Heisenberg Hamiltonian with seven magnetic parameters. Total magnetic energy and orientation of magnetic easy directions were determined for spinel structure of Fe$_3$O$_4$ with octahedral and tetrahedral sites. The effect of number of spin layers and stress induced anisotropy on magnetic properties was investigated. 3-D plot of energy versus angle and number of spin layers was plotted to determine the number of spin layers corresponding to minimum magnetic energy. Magnetic easy axis was found by plotting a graph of energy versus angle for one particular value of the previously-mentioned number of spin layers. Similarly, 3-D and 2-D graphs were plotted for stress induced anisotropy. For film with 4 spin layers, magnetic easy directions were found to be $\theta = 2.3, 2.5, 5.6$ radians, …. When the ratio of stress induced anisotropy to strength of long-range dipole interaction is 2, magnetic easy direction was found to be $\theta = 2.6$ radians. Here the angles were measured with respect to a line drawn normal to the film plane. Because Fe$_3$O$_4$ is a soft magnetic material, Fe$_3$O$_4$ finds potential applications in magnetic memory devices.

Keywords: Third order perturbation, Heisenberg Hamiltonian, ferrites, Fe$_3$O$_4$, easy direction.

INTRODUCTION

Fe$_3$O$_4$ is a prime candidate in applications of magnetic storage, industrial catalysts, water purification and drug delivery. Fe$_3$O$_4$ is a ferrite with inverse spinel structure. Spinel structure with tetrahedral and octahedral sites can be found in detail in some previous publications (Ahmed Farag et al., 2001a; Ahmed Farag et al., 2001b; Kahlenberg et al., 2001; John Zhang et al., 1998; Sickafus et al., 1999). The spinel structure of this ferrite is represented by Fe$^{3+}$Fe$^{2+}$Fe$^{3+}$O$_4$. The magnetic moments of Fe$^{3+}$ and Fe$^{2+}$ are 4 $\mu_B$ and 5 $\mu_B$, respectively. Five of Fe$^{3+}$ ions occupy tetrahedral sites. Other five Fe$^{3+}$ ions and four Fe$^{2+}$ ions occupy octahedral sites. Because magnetic moments of Fe$^{3+}$ in tetrahedral and octahedral sites cancel each other, the net magnetic moment of Fe$_3$O$_4$ is completely due to the magnetic moments of four Fe$^{2+}$ ions. Therefore, the theoretical net magnetic moment of Fe$_3$O$_4$ is 4 Bohr magnetons. However, experimental value of net magnetic moment is approximately 4.1 Bohr magnetons.

Rietveld method has been applied to find cation distribution of ferrite like compounds (Ahmed Farag et al., 2001a, Ahmed Farag et al., 2001b). Surface spin waves in CsCl type ferrimagnet with a (001) surface has been studied by combining Green function theory with the transfer matrix method (Dai and Li, 1990). Anisotropy of ultrathin ferromagnetic films and the spin reorientation transition have been investigated using Heisenberg Hamiltonian with few terms (Usadel and Hucht, 2002). In addition, the surface magnetism of ferrimagnet thin films has been studied using Heisenberg method (Ding et al., 1993). The surface spin wave spectra of both the simple cubic and body centered ferrimagnets have been theoretically studied using Heisenberg Hamiltonian (Hung et al., 1975). The cation distribution and oxidation state of Mn-Fe spinel nanoparticles have been systematically studied at various temperatures by using neutron diffraction and electron energy loss spectroscopy (John Zang et al., 1998). The crystal structure of spinel type compounds has been found using single crystal X-ray diffraction data (Kahlenberg et al., 2001). Surface spin waves on the (001) free surface of semi-infinite two lattice ferrimagnets on the Heisenberg model with nearest neighbor exchange interactions has been investigated (Zheng and Lin, 1988). The lattice parameter, anion parameter and the cation inversion parameter of spinel structures have been found (Sickafus et al., 1999).

Ferromagnetic ultra thin and thick films have been studied using third order perturbed Heisenberg Hamiltonian (Samarasekara, 2008; Samarasekara and Mendoza, 2010). Previously, ferromagnetic ultra-thin and thick films have been investigated using second order perturbed Heisenberg Hamiltonian by us (Samarasekara and Gunawardhane, 2011). Furthermore, ferrite ultra-thin and thick films have been investigated using second order perturbed Heisenberg Hamiltonian by us (Samarasekara et al., 2009, Samarasekara et al., 2010). Ferrite ultra-thin and thick films have been investigated using third order perturbed Heisenberg Hamiltonian by us (Samarasekara and Mendoza, 2011; Samarasekara, 2011). In this manuscript, the third order perturbed Heisenberg Hamiltonian was employed to find the magnetic properties of Fe$_3$O$_4$ thick films.

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MODEL

The modified Heisenberg Hamiltonian of a thin film can be written as following.

\[
H = - J \sum_{\mathbf{r},\mathbf{r}'} \langle \mathbf{S}_\mathbf{r} \cdot \mathbf{S}_{\mathbf{r}'} \rangle + \theta \sum_{\mathbf{r},\mathbf{r}'} \frac{3 \langle \mathbf{S}_\mathbf{r} \cdot \mathbf{S}_{\mathbf{r}'} \mathbf{\hat{r}} \cdot \mathbf{S}_\mathbf{r} \rangle}{r_{\mathbf{r}\mathbf{r}'}} 
- \sum_{\mathbf{r}} D^{(2)}(S^z_{\mathbf{r}})^2 - \sum_{\mathbf{r}} D^{(4)}(S^z_{\mathbf{r}})^4 
- \sum_{\mathbf{r}} H \cdot \mathbf{S}_{\mathbf{r}} - \sum_{\mathbf{r}} K_1 \sin 2\theta_m 
\]

Here \( J, w, q, D^{(2)}, D^{(4)}, H_N, H_{out}, K_1, m, n \) and \( N \) are spin exchange interaction, strength of long range dipole interaction, azimuthal angle of spin, second and fourth order anisotropy constants, in plane and out of plane applied magnetic fields, stress induced anisotropy constant, spin plane indices and total number of layers in film, respectively. When the stress applies normal to the film plane, the angle between \( m^{th} \) spin and the stress is \( q_m \).

The cubic cell has been divided into 8 spin layers with alternative A and Fe spins layers. The spins of A and Fe will be taken as 1 and \( p \), respectively. While the spins in one layer point in one direction, spins in adjacent layers point in opposite directions. A thin film with (001) spinel cubic cell orientation will be considered. The length of one side of unit cell will be taken as \( a \). Within the cell the spins orient in one direction due to the super exchange interaction between spins (or magnetic moments). Therefore the results proven for oriented case in one of our early reports will be used for following equations (Samarasekara et al., 2009) but the angle \( q \) will vary from \( q_m \) to \( q_{m+1} \) at the interface between two cells.

For a thin film with thickness \( Na \),

Spin exchange interaction energy =

\[
E_{\text{exchange}} = N(-10J + 72Jp - 22Jp^2) + 8Jp \sum_{n=1}^{N} \cos(\theta_m - \theta_n) 
\]

Dipole interaction energy = \( E_{\text{dipole}} \)

\[
E_{\text{dipole}} = -48.415 J \sum_{n=1}^{N} \left[ 0 + 3 \cos 2\theta_m \right] 
+ 20.41Jp \sum_{n=1}^{N} \left[ \cos(\theta_m - \theta_n) + 3 \cos(\theta_m + \theta_n) \right] 
\]

Here the first and second term in each above equation represent the variation of energy within the cell and the interface of the cell, respectively. Then total energy is given by

\[
E = N(-10J + 72Jp - 22Jp^2) + 8Jp \sum_{n=1}^{N} \cos(\theta_m - \theta_n) 
- 48.415 J \sum_{n=1}^{N} \left[ 0 + 3 \cos 2\theta_m \right] 
+ 20.41Jp \sum_{n=1}^{N} \left[ \cos(\theta_m - \theta_n) + 3 \cos(\theta_m + \theta_n) \right] 
\]

\[
- \sum_{n=1}^{N} D^{(2)} \cos^2 \theta_n - D^{(4)} \cos^4 \theta_n 
- 4(1-p) \sum_{n=1}^{N} \left[ H_{in} \sin \theta_n + H_{out} \cos \theta_n + K_1 \sin 2\theta_n \right] 
\]

Here the anisotropy energy term and the last term have been explained in our previous report for oriented spinel ferrites. If the angle is given by \( \theta_n = \theta_m + e_m \) with perturbation \( e_m \), after taking the terms up to third order perturbation of \( e_m \).

The total energy can be given as

\[
E(\theta) = E_0 + E(e_1) + E(e_2) + E(e_3) 
\]

where

\[
E_0 = -10JN + 72JpN - 22Jp^2N + 8Jp(N-1) - 48.415JN - 145.245JoN - 154.210JpN + 20.410Jp(N-1) - 4 \sin 2\theta_m 
\]

\[
E(e_1) = -4Jp \sum_{n=1}^{N} \left[ \epsilon_n \right] - 10.2Jp \sum_{n=1}^{N} \left[ \epsilon_n \right] - 193.666 \omega \sin 2\theta_m \sum_{n=1}^{N} \epsilon_n 
\]

\[
- \frac{4}{3} \cos 2\theta_m \sum_{n=1}^{N} D^{(2)} \epsilon_n 
- 4 \frac{\cos^2 \theta_m}{5} \sum_{n=1}^{N} D^{(4)} \epsilon_n 
- 4(1-p) \frac{H_{in} \sin \theta_m}{6} \sum_{n=1}^{N} \epsilon_n + \frac{4K_1}{3} \cos 2\theta_m \sum_{n=1}^{N} \epsilon_n 
\]

The sin and cosine terms in equation number 2 have been expanded to obtain above equations. Here \( n = m + 1 \).

Under the constraint \( \sum_{n=1}^{N} \epsilon_n = 0 \), first and last three terms of equation 4 are zero.

Therefore, \( E(e_1) = \bar{\alpha} \bar{\epsilon} \bar{\epsilon} \).
Here $\alpha(\varepsilon) = \vec{B}(\theta) \sin 2\theta$ are the terms of matrices with
\begin{equation}
B_2(\theta) = -122.46\alpha p + D_4^{(1)} + 2D_4^{(4)} \cos^2 \theta
\end{equation}

Also $E(e^2) = \frac{1}{2} \varepsilon C \varepsilon$, and matrix $C$ is assumed to be symmetric ($C_{nm} = C_{mn}$).

Here the elements of matrix $C$ can be given as following,
\begin{equation}
C_{mm} = -8Jp-20.4\alpha p -61.2p w \cos(2\alpha) +581 \cos(2\alpha)
\end{equation}

For $m = 2, 3, \ldots, N-1$
\begin{align*}
C_{nm} = & -16Jp-40.8\alpha p-122.4\alpha p \cos(2\alpha) +581 \alpha \cos(2\alpha)
\end{align*}

Otherwise, $C_{nm} = 0$

Also $E(e^2) = \varepsilon \beta \varepsilon$

Here matrix elements of matrix $\beta$ can be given as following.

When $m = 1$ and $N$
\begin{equation}
\beta_{mm} = -193.66 \alpha p \sin 2\theta + 10.2 p w \sin 2\theta - \frac{4}{3} \cos \theta \sin \theta
\end{equation}

When $m = 2, 3, \ldots, N-1$
\begin{equation}
\beta_{mm} = -193.66 \alpha p \sin 2\theta + 20.4 p w \sin 2\theta - \frac{4}{3} \cos \theta \sin \theta
\end{equation}

Otherwise $\beta_{mm} = 0$. Also $\beta_{mm} = \beta_{nm}$ and matrix $\beta$ is symmetric.

Therefore, the total magnetic energy given in equation 2 can be deduced to
\begin{equation}
E(\theta) = E_0 + \frac{1}{2} \varepsilon C \varepsilon + \alpha \beta \varepsilon
\end{equation}

Because the derivation of a final equation for $\varepsilon$ with the third order of $\varepsilon$ in above equation is tedious, only the second order of $\varepsilon$ will be considered for following derivation.

Then $E(\theta) = E_0 + \frac{1}{2} \varepsilon C \varepsilon$

Using a suitable constraint in above equation, it is possible to show that $\varepsilon = -\beta^* \alpha$

Here $\beta^*$ is the pseudo-inverse given by
\begin{equation}
C \beta^* = \frac{1}{N}
\end{equation}

$E$ is the matrix with all elements given by $E_{mm} = 1$.

After using $e$ in equation 9,
\begin{equation}
E(q) = E_0 - \frac{1}{2} \varepsilon C \beta^* (C^* \alpha) \varepsilon
\end{equation}

RESULTS AND DISCUSSION

When $N$ is very large (Ex: $N=10000$), $C C^* = 1$, and $C^*$ is the standard inverse matrix of $C$. When the difference between $m$ and $n$ is one, $C_{m,m+1} = 8Jp+20.4\alpha p \cos(2\alpha)$. If $H_{in}$, $H_{out}$ and $K_s$ are very large, then $C_{ij} >> C_{jj}$. If this $C_{m,m+1} = 0$, then the matrix $C$ becomes diagonal, and the elements of inverse matrix $C^*$ is given by $C_{mm}^{-1} = \frac{1}{C_{mm}}$.

Therefore, all the derivation will be done under the above assumption for the convenience.

Then
\begin{equation}
\alpha_{i} = \frac{-\alpha}{\cdot} = \alpha = [-122.46\alpha p + D_4^{(1)} + 2D_4^{(4)} \cos^2 \theta] \sin(2\theta)
\end{equation}

\begin{equation}
\alpha C^* \alpha = 2C^*_{11} \alpha_{i}^2 + \alpha_{i}^2 (N-2) C_{12}^* = \frac{2\alpha_{i}^2}{C_{11}} + \frac{\alpha_{i}^2 (N-2)}{C_{12}}
\end{equation}

For $Fe_2O_4$, $p = 5/4 = 1.25$,
\begin{equation}
E_0 = 55.625JN-10.448.415oN-187.4250N\cos(2\alpha) + 25.5125o(N-1)/1 + 3\cos(2\alpha)
\end{equation}

\begin{equation}
E_0 = -N[\cos^2 \theta D_4^{(2)} + \cos \theta \sin \theta D_4^{(4)}]
\end{equation}

\begin{equation}
C_{ij} = C_{nn} = -10J-25.5o + 504.5ocos(2\alpha) + 2cos 2\theta D_4^{(2)}
\end{equation}

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\end{equation}

\begin{equation}
\alpha^2 = \alpha_{i}^2 (N-2) C_{12}^* = \frac{2\alpha_{i}^2}{C_{11}} + \frac{\alpha_{i}^2 (N-2)}{C_{12}}
\end{equation}
Figure 1 shows the 3-D plot of \( \frac{E(\theta)}{\omega} \) versus \( \theta \) and \( N \).

Maxima of this graph can be observed at \( N = 2.5, 5.5, 8.5, \ldots \) etc. Minima can be observed at \( N = 4, 6.5, \ldots \) etc. Energy minima and maxima correspond to magnetic easy and hard directions. This implies that the films can be easily magnetized for some particular values of \( N \). In addition, the effect of deposition temperature on magnetic easy axis orientation can be explained using Heisenberg Hamiltonian and spin reorientation (Samarasekara and Gunawardhane 2011; Samarasekara and Saparamadu, 2012; Samarasekara and Saparamadu, 2013). Although this 3-D plot is exactly the same as that of ferromagnetic thick films found using third order perturbed Heisenberg Hamiltonian, the maximum energy in this 3-D plot is slightly higher than that of ferromagnetic thick film (Samarasekara, 2008). This 3-D plot is similar to that of thick nickel ferrite films obtained using the second order perturbation (Samarasekara, 2010).

Figure 2 shows the graph of energy versus angle for \( N = 4 \). Energy maxima can be observed at \( \theta = 0, 0.4, 3.6 \) radians, \( \ldots \) etc. Energy minima can be observed at \( \theta = 2.3, 2.5, 5.6 \) radians, \( \ldots \) etc. Therefore, magnetic easy directions are \( \theta = 2.3, 2.5, 5.6 \) radians, \( \ldots \) etc. This curve is somewhat similar to the same curve obtained for nickel ferrite thick films using third order perturbed Heisenberg Hamiltonian (Samarasekara, 2011).
Figure 2: Graph of energy versus angle for $N = 4$.

Figure 3: 3-D plot of $\frac{E(\theta)}{\omega}$ versus $\theta$ and $K_s$.

Figure 3 shows the 3-D plot of $\frac{E(\theta)}{\omega}$ versus $\theta$

and $K_s$ for $\frac{J}{\omega} = \frac{D_s}{\omega} = \frac{H_s}{\omega} = \frac{H_{sat}}{\omega} = 0$

and $\frac{D_s}{\omega} = 5$. Here $N = 10000$. Energy maxima can be
observed at $\frac{K_s}{\omega} = 5, 9.5, 14, \ldots$ etc. Energy minima can
be observed at $\frac{K_s}{\omega} = 2, 6, 10, \ldots$ etc. This means that the
film can be easily magnetized in some particular directions by applying a particular value of stress. Stress induced anisotropy arises in the film during heating or cooling due to the mismatch between thermal expansion coefficients of substrate and the film. This 3-D plot is entirely different from that of thin ferrite films obtained using second order perturbed Heisenberg Hamiltonian (Samarasekara et al., 2009). In addition, this 3-D plot is different from that of thin ferromagnetic films with three spin layers plotted using third order perturbed Heisenberg Hamiltonian (Samarasekara and Mendoza, 2010). But the total energy of the thick film is much higher than that of ultra thin film.
Figure 4 shows the graph of $\frac{E(\theta)}{\omega}$ versus angle for $K_s = 2$. Energy minima can be observed at 2.6 radians. Compared to this curve, smooth sine curves could be obtained for ferrite ultra thin films using third order perturbed Heisenberg Hamiltonian (Samarasekara and Mendoza, 2011). According to our experimental studies of nickel ferrite films, the magnetic properties depend on the stress induced anisotropy of the film (Samarasekara and Cadieu, 2001).

CONCLUSION

According to the 3-D plot of energy versus angle and number of spin layers, Fe$_3$O$_4$ thick film can be easily magnetized at some particular values of number of spin layers along some particular directions. When $N = 4$, 6, 5, ... etc, total magnetic energy becomes minimum. Magnetic easy directions were found to be $\theta = 2.3$, 2.5, 5.6 radians, ... etc as measured with respect to a line drawn normal to the film plane for $N = 4$. Similarly, magnetic hard directions were found to be $\theta = 0.4$, 3.6 radians, ... etc for this case. According to the 3-D plot of energy versus angle and stress induced anisotropy, Fe$_3$O$_4$ thick films can be easily magnetized at some particular values of stress induced anisotropy. When $\frac{K_s}{\omega} = 2, 6, 10, ...$ etc, total magnetic energy becomes a minimum. Magnetic easy direction was found to be $\theta = 2.6$ radians as measured with respect to a line drawn normal to the film plane for $\frac{K_s}{\omega} = 2$.

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