STUDY OF MAGNETIZATION VARIATION IN MAGNETIC NANOMATERIALS HAVING WIDE APPLICATIONS IN MAKING ANTI-CORROSION COATINGS USING QUALITATIVE APPROACH

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SUMMARY

Nanostructured magnetic nanoparticles and nanocomposites possess exceptional properties and serve and act as an interface between physics and engineering. Innovations in nano-scale material science can be utilized to solve the issue of marine biofouling by creating anti-corrosion coatings that are not harmful to wildlife and the environment. In this paper, the author has studied the impact of size, dimension, and shape on the Saturation magnetisation of magnetic nanomaterials having wide applications using a qualitative model. It is known that Curie temperature and saturation magnetisation of magnetic materials are linearly related and also the Curie temperature varies linearly with melting temperature. A qualitative model is proposed in the present study extending the relation between Curie temperature and Saturation magnetisation to study the size and shape effect on magnetisation (MS) in nano solids. The nanomaterials considered to study the size and shape impact on Saturation magnetisation with size are Fe, Ni, Co, Fe_3O_4, $MnFe_2O_4$, and $CoFe_2O_4$. The Saturation magnetisation is found to reduce with size reduction at nano level due to the drastic increase in the surface area to volume ratio in nano solids with size reduction to nanoregime. The results obtained using the model are compared with the available experimental data. The variation in magnetisation is studied for shapes viz. nanowires, thin films, spherical, tetrahedral, octahedral, dodecahedral and icosahedral nanosolids. A good consistency is obtained between the present model results and the experimental results available that justify the validity of the model proposed.

KEYWORDS

Magnetization, Curie temperature, Size, Shape, Dimension

1. INTRODUCTION

Nanotechnology is an emerging multidisciplinary area of research that has drawn the attention of scientists and researchers worldwide over the past few decades. Nanomaterials have unique and fascinating properties that are found different from their counterpart bulk form. For the past few decades, magnetic nanomaterials have been fabricated using different experimental methods which help in exploring their properties and characteristic behaviour [1-4]. It has been found that size, shape, and dimension all have a great impact on the properties of nanomaterials. Nanotechnology has proved to be a valuable tool that can help in cleaning up oil spills in the water by utilizing magnetic nanomaterials such as functionalized super-paramagnetic iron oxide nanoparticles and magnetic nanocomposites. Nanostructured magnetic nanoparticles and nanocomposites possess exceptional properties that are used to treat oily wastewater. Because of their outstanding properties, Magnetic nanoparticles can be applied in multidisciplinary areas and create hope for a bright future to address emerging biomedical and environmental challenges [5, 6].

Magnetic materials having low dimensions viz. nanorods, thin films, multilayers, etc. are found to be the multidisciplinary subjects of research due to their applications in different fields. The enormous increase in surface atoms in nanomaterials depicts the dependence of size, dimension, and shape on their properties. As size reduction takes place in magnetic materials, the thermo physical behaviour shown by them varies [7-10].

Magnetic nanoparticles have applications in wide areas viz. ultra-high frequency devices, drug carriers in specific site drug delivery, colour imaging, ferrofluids, and magnetic refrigeration, etc. [11,12]. Cobalt ferrite $CoFe_2O_4$, a magnetic nanomaterial, is used to produce isotropic permanent magnet and magnetic recording as it has large magnetic hysteresis in comparison to other spinel ferrites [13]. Manganese spinel ferrite $MnFe_2O_4$ nanoparticles work as contrast enhancement agents in the Magnetic resonance imaging (MRI) technique. It is noted from previous studies that magnetic nanoparticles usually possess a single domain structure and exhibit phenomena like super-paramagnetism [14, 15]. The decrease in Curie temperature in ferromagnetic nanomaterials with a decrease in size is studied both experimentally and theoretically. The properties of ferroelectric materials are also found to be influenced by size reduction. Saturation magnetization is the maximum value of magnetization achieved when the material is placed in a large magnetic field. This property is influenced by temperature. At the nanoscale, magnetization is found to decrease with size reduction at room temperature [16-19].

Many experiments have been carried out to fabricate nanomaterials and explore their properties with respect to size and temperature. In addition, Simulations and theoretical qualitative and quantitative models have been developed to study the properties of magnetic nanomaterials. Zhong et al. [20] used the bond-order-length-strength (BOLS) correlation method to study the Magnetization in ferromagnetic nanosolids. Jiang et al. [21] investigated the size effect on the Saturation magnetisation of ferromagnetic nanocrystals using a cohesive energy model. He et al. [22] used both experimental and theoretical methods to study the magnetic properties of Ni nanoparticles.

In the present paper, a qualitative model is used to study the impact of size, shape and dimension on the Saturation magnetisation of ferromagnetic and ferrimagnetic nanomaterials. The nanomaterials considered are Fe, Ni, Co, γ-Fe_2O_3, $MnFe_2O_4$, and $CoFe_2O_4$. Magnetic nanoparticles also include the group of metallic nanoparticles and nanoalloys.

2. MATHEMATICAL FORMULATION

Using the known fact that the bond energy of a solid is linearly related to its cohesive energy [23,24]; Cohesive energy E_{CN} for the nanomaterials is expressed as follows:

$$E_{CN} = \left(\frac{1}{2}n_i\beta_L + \frac{1}{2}n_s\beta_S\right)\varepsilon = \frac{1}{2}\left\{n_t\beta_L - n_s\left(\beta_L - \beta_S\right)\right\}\varepsilon \quad (1)$$

Where n_i ; n_s ; n_t stand for the number of interior atoms, number of surface atoms, and total number of atoms in nanomaterial. Energy for each bond is taken as ε . β_L represents atoms coordination number in the lattice and β_S in surface crystalline planes. E_{CB} is cohesive energy of bulk solid and is expressed as:

$$E_{CB} = \frac{1}{2}n_t\beta_L\varepsilon \quad (2)$$

Melting temperature and cohesive energy vary directly [23, 24]; therefore, the ratio of cohesive energy of nanomaterial to bulk is taken equal to the melting temperatures of nanosolid (T_{MN}) to its bulk form (T_{MB}) and the relation so obtained is expressed as follows:

$$\frac{E_{CN}}{E_{CB}} = \frac{T_{MN}}{T_{MB}} = \frac{n_t\beta_L - n_s\left(\beta_L - \beta_S\right)}{n_t\beta_L} = 1 - \frac{\left(\beta_L - \beta_S\right)}{\beta_L}\frac{n_s}{n_t} \quad (3)$$

Considering $q = \frac{\beta_S}{\beta_L}$; eq. (3) can be written as:

$$\frac{T_{MN}}{T_{MB}} = 1 - \left(1 - q\right)\frac{n_s}{n_t} \quad (4)$$

Lindemann criterion [25] relates melting temperature T_M and Debye temperature θ_D as folllows:

$$\theta_D = C\left(\frac{T_M}{MV^{2/3}}\right)^{1/2} \quad (5)$$

where C is constant.

In view of equations (4, 5); Debye temperature of nanosolid θ_{DN} and corresponding bulk θ_{DB} are related as follows:

$$\theta_{DN} = \theta_{DB}\left\{1 - \left(1 - q\right)\frac{n_s}{n_t}\right\}^{1/2} \quad (6)$$

If the structure of ferromagnetic and antiferromagnetic nanocrystals is the same as that of the bulk form, the relation between Curie temperature T_C and Debye temperature θ_D can be written as follows [21, 26]:

$$\frac{T_{CN}}{T_{CB}} = \frac{\theta_{DN}^{\ 2}}{\theta_{DB}^{\ 2}} \quad (7)$$

Here, T_{CN} ; T_{CB} are Curie temperatures for nanomaterial and corresponding bulk respectively.

Liang and Baowen [27] relate melting temperature and Debye temperature as follows [27]:

$$\frac{T_{MN}}{T_{MB}} = \frac{\theta_{Dn}^{\ 2}}{\theta_{Db}^{\ 2}} \quad (8)$$

Combining equations (6-8); Curie temperature of nano solid to its bulk form can be expressed as:

$$\frac{T_{MN}}{T_{MB}} = \frac{T_{CN}}{T_{CB}} = 1 - \left(1 - q\right)\frac{n_s}{n_t} \quad (9)$$

Magnetisation explains the effect of an external magnetic field on the material and it causes the dipoles within the material to align with the direction of an external field. For

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ferromagnetic materials, the Curie temperature is related to magnetisation as follows [21]:

$$\frac{M_N}{M_B} = 4\left[\frac{T_{CN}}{T_{CB}}\right] - 3 \qquad (10)$$

Where M_N, M_B are saturation magnetisation for nanosolid and its corresponding bulk material.

Equation (10) depicts that the suppression in magnetisation is about four times to that of T_c. Using equation (9) in equation (10), the ratio of magnetisation in nano to its bulk form of material is expressed as follows:

$$\frac{M_N}{M_B} = 4\left\{1 - (1-q)\frac{n_s}{n_t}\right\} - 3 \qquad (11)$$

Qi [28] reported a simple method to determine the express the ratio of number of surface atoms to total atoms (n_s/n_t) in nanostructure in terms of size of the nanostructure. For spherical nanoparticles, if D the diameter of spherical nanoparticle and d as atomic diameter [28-31]; n_s and n_t are found as follows:

$$n_s = \frac{4S'}{\pi d^2} = 4\frac{D^2}{d^2}\,;\, n_t = \frac{4\pi D^3/3}{4\pi d^3/3} \qquad (12)$$

or

For spherical naoparticles: $\frac{n_s}{n_t} = \frac{4d}{D}$ (13)

Similarly,

For thin Film: $\frac{n_s}{n_t} = \frac{4d}{3h}$ (14)

For cylindrical Wire: $\frac{n_s}{n_t} = \frac{8d}{3L}$ (15)

For Hexahedral shape: $\frac{n_s}{n_t} = \frac{4d}{a}$ (16)

For Octahedral shape: $\frac{n_s}{n_t} = \frac{4.898d}{a}$ (17)

For Tetrahedral shape: $\frac{n_s}{n_t} = \frac{9.797d}{a}$ (18)

For Dodecahedral shape: $\frac{n_s}{n_t} = \frac{1.796d}{a}$ (19)

For Icosahedral shape: $\frac{n_s}{n_t} = \frac{2.646d}{a}$ (20)

Where size of nanostructure depending on its shape is D, h, L and a as taken in equations (13-20).

3. RESULTS AND DISCUSSION

The author has formulated a simple qualitative model free from any approximations to study the impact of size and shape on saturation magnetization in ferromagnetic and ferrimagnetic nanocrystals. The study is done at room temperature. The input parameter required in the calculation is the atomic diameter of the material which is listed in Table 1. The ratio of the number of surface atoms to total atoms in nanosolid n_s/n_t for different shapes of nanostructures is expressed in terms of the size of the nanostructure as shown in equations (13-20). The value of n_s/n_t depends on atomic diameter and it varies with the size of the nano solid. The variation in saturation magnetization with size is studied using equation (11) for nanomaterials, nanowires, thin films, and other shapes. The nanomaterials considered for studying the variation of the saturation magnetization with size are Fe, Ni, Co, Fe_3O_4, $MnFe_2O_4$, and $CoFe_2O_4$. The model results obtained are compared with experimental data available to verify the suitability of the present model.

Curie temperature as well as saturation magnetisation is considered to vary with the size of the nanostructure. As it is discussed magnetization **(**M_S**)** is related to Curie

Table 1. Input parameter required [21]

S. No.	Material	d(nm)
1.	F	**0.2482**
2.	Ni	**0.2492**
3.	Co	**0.2506**
4.	$MnFe_2O_4$	**0.2293**
5.	$CoFe_2O_4$	**0.2264**
6.	Fe_3O_4	**0.1890**

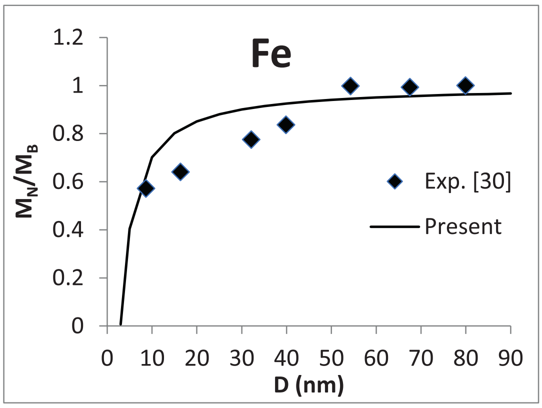

Figure 1. Relative magnetization versus diameter in Fe (Sphere) nanomaterial

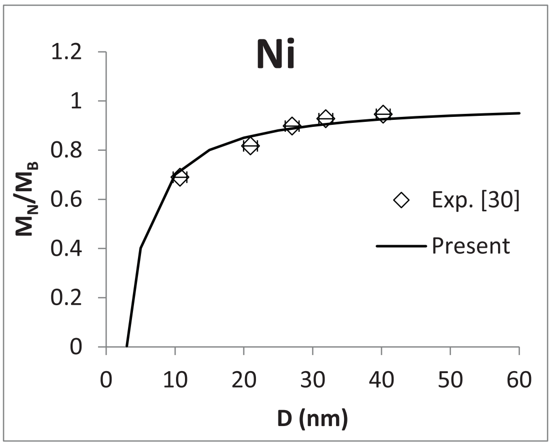

Figure 2. Relative magnetization versus diameter in Ni (Sphere) nanomaterial

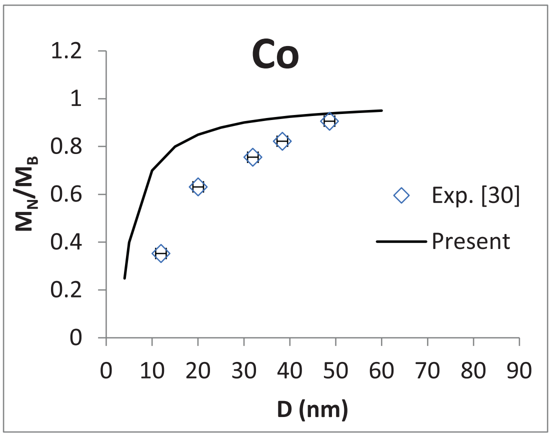

Figure 3. Relative magnetization versus diameter in Co (Sphere) nanomaterial

temperature (**T_C**) so the expression of Curie temperature (eq. 9) is extended to obtain the relation of saturation magnetization with the size of the nanosolid. The variation of magnetization with size is studied using the present model equation (11). Depending on the shape of the nanostructure, the ratio n_s/n_t varies. The value of q lies between $0 < q < 1$.

Figure 1 depicts relative saturation magnetization M_N/M_B variation with size for spherical nanoparticles of Fe. It is noted from the Figure plotted that M_N/M_B decreases with the reduction in the size of nanosolid. It is clear from eq. (10) that suppression in magnetisation is about four times of the T_C and it is the result of the rapid increase in surface atoms as the size of the nanomaterial decreases. With an increase in surface atoms in nano solids, there is a drop in the exchange interaction energy and inter-spin interaction get weakened leading to a reduction in magnetization with a reduction in the size of nano solid. Figures 2-7 depict the relative saturation magnetization M_N/M_B variation with size in spherical nanoparticles of Ni, Co, γ-Fe_2O_3, $MnFe_2O_4$, and $CoFe_2O_4$ and thin film of Ni. The value of q i.e., the ratio of ${}^{\beta_S}/_{\beta_L}$ is taken as ¼ in model calculations. The obtained results are compared with the experimental data available [30-39] for Fe, Ni, Co, Fe_3O_4, $MnFe_2O_4$, and $CoFe_2O_4$ nanosolids and Ni thin film.

It is noted from the graphs plotted that the predicted model results from the model calculations are in good accordance with the experimental data available [30-39] as depicted in the figures plotted. There are some deviations in compared results for Fe, Ni and Co for the small size of the nanosolid as there may be some experimental errors in calculated results and also the model has certain limitations. Figures (1-7) are plotted to study the variation of magnetization in nanosolids with size.

Variation of magnetization with size is studied for nanomaterials of different shapes. It is clear from the study that with the change in the shape of the nanomaterial, the ratio of the number of surface atoms to the total number of atoms in it changes leading to a change in magnetization value. It is found that the magnetization increases with an increase in the size of the nanomaterial and a rapid increase in magnetization is observed with an increase in the thickness of nanofilms as compared to other shapes of nanomaterial.

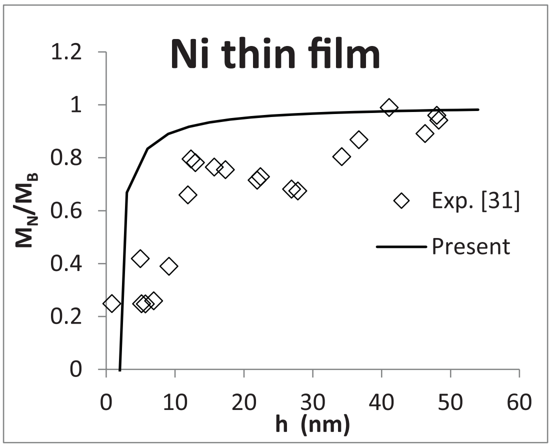

Figure 4. Relative magnetization versus size in Ni (thin film)

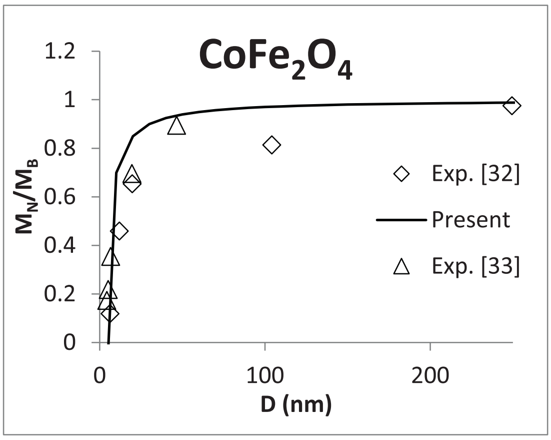

Figure 5. Relative magnetization versus diameter in $CoFe_2O_4$ (Sphere) nanomaterial

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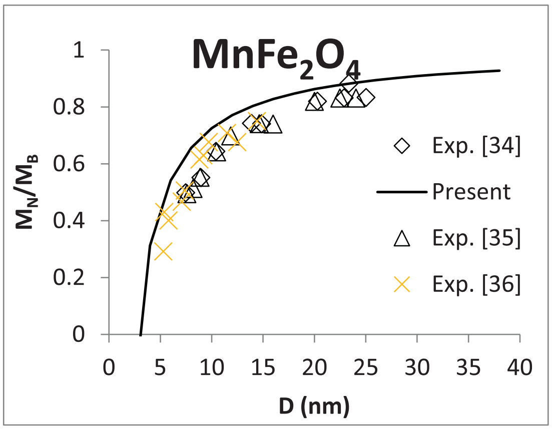

Figure 6. Relative magnetization versus diameter in $MnFe_2O_4$ (Sphere) nanomaterial

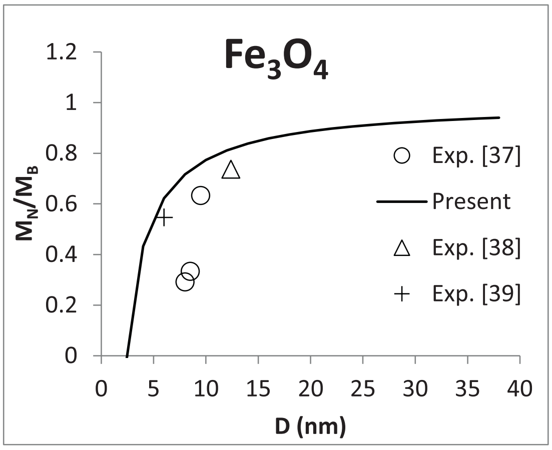

Figure 7. Relative magnetization versus diameter in Fe_3O_4 (Sphere) nanomaterial

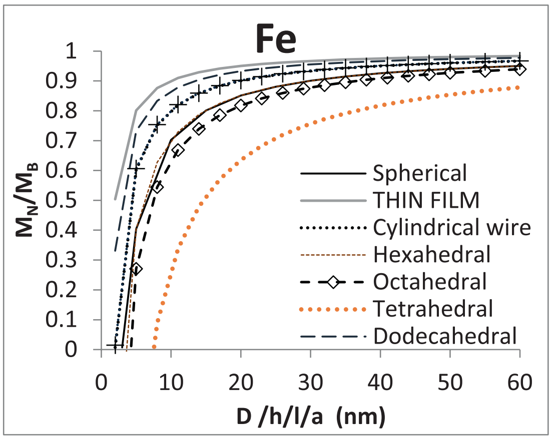

Figure 8. Relative magnetization with size for Fe nanosolid of different shapes

Figure 8 depicts the variation of magnetization with size in Fe nanosolids in the shape of cylindrical nanowires, thin film, spherical, tetrahedral, octahedral, dodecahedral, and icosahedral nanoparticles**.** It is clear from the figure plotted that with a change in shape, there is an increase or decrease in the surface atoms in nanosolids which results in a change in the magnetization. Drop in magnetization value with decrement in size in maximum in tetrahedral nanoparticles. The shape effect is found more noticeable for the nanosolids of size less than 20 nm. Due to a drastic increase in the surface-to-volume ratio for size below 20 nm, there is a sudden drop in magnetization compared to bulk material.

It can be said that the anomalous and rapid change in the magnetic behavior of nanomaterial is due to the large surface-to-volume ratio at the nanolevel. The present study may provide the estimated values of magnetization to the researchers setting up experimental methods for the Synthesis and characterization of magnetic nanomaterials by providing them insight into their magnetic behavior. Surface coatings of magnetic nanoparticles possess improved stability and solubility that increase their biocompatibility, and target-specificity, and prevent them from oxidation, corrosion, and toxicity [42].

4. CONCLUSIONS

The present study gives an overview of the magnetic properties of magnetic nanomaterials that can have wide applications in the creation of anti-corrosion coatings that are environment-friendly and can be used to solve the issue of marine biofouling. The variation of saturation magnetization in ferromagnetic and ferrimagnetic nanosolids is studied with size and shape using a qualitative model. The model is free from any approximation and considers the variation in surface atoms to total atoms ratio depending upon the shape of nanomaterials. A good agreement between the model-calculated results and available experimental data [32-41] justifies the validity of the present work. The model formulation may be beneficial for researchers who are working experimentally on magnetic nanomaterials.

5. DECLARATION OF COMPETING INTEREST STATEMENT

The author declares that there are no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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