Magnetic Attributes of NiFe$_2$O$_4$ Nanoparticles: Influence of Dysprosium Ions (Dy$^{3+}$) Substitution

Munirah Abdullah Almessiere$^{1,2,*}$, Y. Slimani$^{1,*}$, H. Güngüneş$^3$, S. Ali$^4$, A. Manikandan$^5$, I. Ercan$^1$, A. Baykal$^6$ and A.V. Trukhanov$^7,8,9$

$^1$ Department of Biophysics, Institute for Research & Medical Consultations (IRMC), Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam 31441, Saudi Arabia; iercan@iau.edu.sa
$^2$ Department of Physics, College of Science, Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam 31441, Saudi Arabia
$^3$ Department of Physics, Hitit University, Çeşme Yolu Bulvarı-Çorum 19030, Turkey; gungunes@gmail.com
$^4$ Mechanical and Energy Engineering Department College of Engineering, Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam 31441, Saudi Arabia; sadali@iau.edu.sa
$^5$ Department of Chemistry, Bharath Institute of Higher Education and Research, Bharath University, Chennai, Tamil Nadu 600073, India; manikandana.che@bharathuniv.ac.in
$^6$ Department of Nano-Medicine Research, Institute for Research & Medical Consultations (IRMC), Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam 31441, Saudi Arabia; abaykal@iau.edu.sa
$^7$ Scientific-Practical Materials Research Centre NAS of Belarus, 19 P. Brovki Street, 220072 Minsk, Belarus; truhanov86@mail.ru
$^8$ Department of Electronic Materials Technology, National University of Science and Technology MISiS, Leninsky Prospekt, 4, Moscow 119049, Russia
$^9$ Laboratory of Crystal Growth, South Ural State University, Lenin Prospect, 76, Chelyabinsk 454080, Russia

* Correspondence: malmessiere@iau.edu.sa (M.A.A.); yaslimani@iau.edu.sa (Y.S.);
Tel.: +966-50-580-7292 (M.A.A.); +966-59-965-8876 (Y.S.)

Received: 2 May 2019; Accepted: 28 May 2019; Published: 31 May 2019

Abstract: This paper reports the influence of dysprosium ion (Dy$^{3+}$) substitution on the structural and magnetic properties of Ni$_{2-x}$Dy$_x$Fe$_{2-x}$O$_4$ (0.0 $\leq$ $x$ $\leq$ 0.1) nanoparticles (NPs) prepared using a hydrothermal method. The structure and morphology of the as-synthesized NPs were characterized via X-ray diffraction (XRD), scanning and transmission electron microscope (SEM, and TEM) analyses. $^{57}$Fe Mössbauer spectra were recorded to determine the Dy$^{3+}$ content dependent variation in the line width, isomer shift, quadrupole splitting, and hyperfine magnetic fields. Furthermore, the magnetic properties of the prepared NPs were also investigated by zero-field cooled (ZFC) and field cooled (FC) magnetizations and AC susceptibility measurements. The $M_{ZFC}(T)$ results showed a blocking temperature ($T_B$). Below $T_B$, the products behave as ferromagnetic (FM) and act superparamagnetic (SPM) above $T_B$. The $M_{FC}(T)$ curves indicated the existence of super-spin glass (SSG) behavior below $T_s$ (spin-glass freezing temperature). The AC susceptibility measurements confirmed the existence of the two transition temperatures (i.e., $T_B$ and $T_s$). Numerous models, e.g., Neel–Arrhenius (N–A), Vogel–Fulcher (V–F), and critical slowing down (CSD), were used to investigate the dynamics of the systems. It was found that the Dy substitution enhanced the magnetic interactions.

Keywords: NiFe$_2$O$_4$; spinel ferrites; structure; microstructure; magnetization; AC susceptibility

1. Introduction

Lately, nanosized Ni-spinel ferrites have widely been used in magnetic storage media, magnetic adsorbents, telecommunication, catalysts, microwave absorbers, and computer memories [1–5]. Further, the structural and magnetic characteristics of nanosized Ni-spinel ferrites have been enhanced
by substituting varieties of magnetic, nonmagnetic, and rare earths ions [6–8]. Such improvement was majorly attributed to the distribution of substitution ions between tetrahedral and octahedral sites of the host and eventual influence on their magnetic moments [8]. Moreover, the use of rare earths as substitution agents in the spinel ferrite was found to cause structural distortion through symmetry preserving the lattice strain and thereby modifying the overall properties of nanosized spinel ferrites [9]. Intense research efforts have been made to enhance the structure, optical, and magnetic properties of rare earth ion substituted nanosized Ni-spinel ferrites [2,3]. Meanwhile, different theories and models have been applied to achieve a better understanding of the unique magnetic properties of these doped nanosized Ni-spinel ferrites [2,3]. Modified magnetic properties of Erbium (Er3+) and Samarium (Sm3+) substituted nickel ferrites were analyzed by low temperature magnetization, and zero-field cooled and field cooled (ZFC-FC) measurements. Such samples revealed a superparamagnetic (SPM) behavior with very low coercivity ($H_c$) and remanence magnetization ($M_r$), making them suitable for developing soft magnets [10]. A substitution of Pr, Sm, and La in Ni$_{0.5}$Zn$_{0.5}$Fe$_{1.95}$R$_{0.05}$O$_4$ nanoparticles (NPs) was found to modify their magnetic and dielectric properties [11]. Conversely, Cerium (Ce) substituted Ni-Zn at low contents ($0.0 \leq x \leq 0.1$) produced high saturation magnetization ($M_s$), remanence, and coercivity [12].

So far, studies on Dy3+ substituted nanosized Ni spinel ferrites are rare. J. Sahariya et al. [13] reported the temperature dependent spin momentum densities of NiFe$_{2-x}$RE$_x$O$_4$ ($x = 0, 0.05$ and $RE = Dy, Gd$) ferrites measured by using a magnetic Compton spectrometer. The experimental profiles of NiFe$_2$O$_4$ with doping of Dy and Gd show a similar spin moment to the non-doped sample. The contribution of different constituents in the formation of total spin moment is deduced from the analysis of the Compton line shape. It is seen that Dy$^{3+}$ or Gd$^{3+}$ doping ions at Fe$^{3+}$ sites lead to a redistribution of the spin moment at Fe$^{3+}$ and RE$^{3+}$ sites. The temperature dependent magnetic Compton profiles are decomposed into the constituent profiles of Ni, Fe, Dy/Gd, and diffuse components, arising due to O-2sp states. A decrease in the Fe spin moment from 0.55 ± 0.03 $\mu_B$/f.u. (in NiFe$_2$O$_4$) to 0.41(0.50) ± 0.03 $\mu_B$/f.u. is observed on the partial substitution of Dy(Gd). K. Kamala Bharathi et al. [14] reported a correlation between the microstructure, electrical, and optical properties of Dysprosium-doped nickel-ferrite (NiFe$_{1.925}$Dy$_{0.075}$O$_4$) thin films fabricated using sputter-deposition using a stoichiometric bulk target prepared by a solid-state chemical reaction. Recently, M.A. Almessiere et al. [15] investigated the effects of dysprosium substitution on the structural, microstructural, and magnetic properties of NiFe$_2$O$_4$ nanoparticles. The formation of the cubic phase of Ni nanosized ferrites was confirmed. The magnetic properties were done by analyzing measurements of the magnetization versus applied field $M(H)$. These measurements were carried out at two different temperatures—room temperature ($T = 300$ K) and low temperature ($T = 10$ K). A noticeable improvement in the differently deduced magnetic parameters, including saturation magnetization ($M_s$), remanence ($M_r$), and coercivity ($H_c$), was observed at both room ($T = 300$ K) and low ($T = 10$ K) temperatures with Dy substitution. The increase in the different magnetic parameters is mainly attributed to the strengthening of A–B exchange interactions owing to the substitution of Fe$^{3+}$ ions with Dy$^{3+}$ ions with larger ionic radii, the formation of local strains, and the increase in the magnetic moments ($N_B$).

To the best of our knowledge, there is no study reporting the Mossbauer, zero-field cooled (ZFC), and field cooled (FC) magnetizations and AC susceptibility measurements for Dy substituted nanoparticles of Ni spinel ferrites. Accordingly, we examined in the present study the influence of Dy$^{3+}$ doping on the structure, morphology, Mossbauer, ZFC-FC magnetization, and AC susceptibility of NiDy$_x$Fe$_{2-x}$O$_4$ ($0.0 \leq x \leq 0.1$) nanoparticles. Various products were synthesized using a hydrothermal process.

2. Experimental

Various specimens with the chemical formula NiDy$_x$Fe$_{2-x}$O$_4$ ($0.0 \leq x \leq 0.1$) have been prepared by a hydrothermal process. Analytical grade high purity chemical reagents including Dysprosium III nitrate hydrate (Dy (NO$_3$)$_3$·H$_2$O), Nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O), Iron III nitrate (Fe(NO$_3$)$_3$·9H$_2$O), and Sodium Hydroxide (NaOH) were taken as starting materials. Then, the stoichiometric amount of these compositions was mixed in distilled water and the resulting mixture was left at room temperature.
Next, a clear solution was made for pH adjustment using 2M of NaOH solution and placed in a stainless steel-Teflon autoclave to initiate the hydrothermal treatment. Finally, the obtained sample was dried and grinded for further experimental analyses.

A Rigaku Benchtop Miniflex X-ray diffraction (XRD) diffractometer (Tokyo, Japan) with Cu K$_\alpha$ radiation at room temperature (RT) over a 2$\theta$ range from 20$^\circ$ to 70$^\circ$ was used for the structural analysis. Scanning electron microscopy (SEM, FEI Titan 80–300 kV FEG S/TEM, Hillsboro, OR, USA), along with energy dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM; FEI, Morgagni 268, Prague, Czech Republic), was used for the morphological and composition analyses. AC magnetic susceptibility, zero-field cooled (ZFC), and field cooled (FC) magnetization measurements were performed using a superconducting quantum interference device (PPMS DynaCool, Quantum Design, San Diego, CA, USA). ZFC-FC magnetizations were carried out at a temperature range of 2–400 K under a DC field of 100 Oe. Real and imaginary parts of AC susceptibility measurements were done at temperatures ranging from 350 to 2 K in the presence of an ac applied magnetic field of $H_{ac}$ = 10 Oe and in different frequencies ranging from 50 to 10,000 Hz. Mössbauer spectra were performed at room temperature using a conventional Mössbauer spectrometer (Fast Com Tec PC-moss II, Oberhaching, Germany) under the constant acceleration mode using $^{57}$Fe in an Rh matrix with an approximate activity of 10 m Ci. The speed scale and the velocity were calibrated using $\alpha$-Fe and laser interferometry, respectively. The recorded spectra were analyzed and fit to the inbuilt Win-Normos fitting software (WISSEL company, Duisburg, Germany).

3. Results and Discussion

3.1. Structure

Figure 1 displays the XRD powder patterns of the studied NiDy$_x$Fe$_{2-x}$O$_4$ (0.0 $\leq$ x $\leq$ 0.1) nanoparticles. Irrespective of Dy$^{3+}$ contents, all the XRD peaks have been verified to the cubic nanosized Ni-spinel ferrites (JCPDS Card Number 54-0964), indicating the lattice site compatibility of the Dy$^{3+}$ ions in the Ni spinel ferrite structure in the absence of any impurity. The calculated structural parameters of the prepared nanosized spinel ferrites were enlists in Table 1. It was realized that lattice parameters elongate due to the increase in the substitution contents and also show ionic radii disparity between Fe$^{3+}$ (0.78 Å) and Dy$^{3+}$ (1.03 Å). The calculated crystallite sizes ($D_{XRD}$) were in the range of 24 to 35 nm [16].

![Figure 1. X-ray diffraction (XRD) powder patterns of prepared nanoparticles (NPs).](image)
Table 1. Structural parameters of studied NiDy$_x$Fe$_{2-x}$O$_4$ NPs.

| $x$  | $a$ (Å)  | $V$ (Å$^3$) | $D_{XRD}$ (nm) |
|------|--------|------------|----------------|
| 0.00 | 8.3378 | 579.6451   | 34.7           |
| 0.01 | 8.3397 | 580.0333   | 33.1           |
| 0.03 | 8.3413 | 580.3630   | 34.7           |
| 0.05 | 8.3424 | 580.5463   | 30.8           |
| 0.07 | 8.3473 | 579.3824   | 32.3           |
| 0.09 | 8.3470 | 579.9142   | 33.1           |
| 0.10 | 8.3473 | 580.9998   | 24.3           |

3.2. Morphology

Figure 2 displays the SEM pictures, EDX spectra, and elemental mapping results for $x = 0.01$ and 0.05 samples. The surface morphology of these samples revealed a high degree of nanoparticle agglomeration. EDX analysis proved the existence of appropriate elements (Fe, Ni, Dy, and O) in the samples. Figure 3 illustrates the TEM image of the nanosized spinel ferrites containing Dy$^{3+}$ contents of 0.05. The inset (Figure 3) displays the selected angle electron diffraction (SAED) patterns of the corresponding sample that confirmed the agglomeration of single crystalline Ni spinel ferrite nanoparticles.

![Figure 2](image-url)
3.3. Mössbauer Spectra

Figure 4 depicts the Mössbauer spectra of synthesized NiDy\(_x\)Fe\(_{2-x}\)O\(_4\) (0.0 \(\leq x \leq 0.1\)) NPs at room temperature. Table 2 enlists various Mössbauer parameters calculated by spectral fitting using three sextets (A for the tetrahedral sites and B and B\(_1\) for the octahedral sites). Fe\(^{3+}\) ions in the tetrahedral A site are characterized by a large hyperfine field with an insignificant isomer shift. Conversely, the other two sextets with a comparatively smaller hyperfine field signify the occupation of Fe\(^{3+}\) at two dissimilar environments in the B-site [17]. Besides the ferromagnetic sextets, a minute paramagnetic doublet with quadrupole-splitting was evidenced for NiDy\(_{0.01}\)Fe\(_{1.99}\)O\(_4\), NiDy\(_{0.07}\)Fe\(_{1.93}\)O\(_4\), and NiDy\(_{0.1}\)Fe\(_{1.9}\)O\(_4\) NPs. The occurrence of such a paramagnetic doublet was attributed to the fractions of Fe\(^{3+}\) with fewer nearest neighbors that possessed magnetically ordered spins. Interestingly, in the spinel ferrite structure, Fe\(^{3+}\) did not contribute to the super exchange interaction [18].

Figure 4. Mössbauer spectra of studied NPs.
Table 2. Evaluated Mössbauer parameters of studied ferrite NPs (B_{hf}: hyperfine magnetic field, I.S.: isomer shift, Q.S.: quadrupole splitting, W: line width, and R_A: Relative area).

| x   | Assignment of Sites | I.S. (±0.002) (mm/s) | Q.S. (±0.004) (mm/s) | B_{hf} (±0.02) (T) | W (±0.01) (mm/s) | R_A (%) | Cation Distribution |
|-----|---------------------|-----------------------|----------------------|---------------------|------------------|---------|---------------------|
| 0.01| Sx-A: Fe^{3+}       | 0.368                 | 0.005                | 52.045              | 0.218            | 17.298  | (Ni_{0.65}Fe_{0.35})_{A} [Ni_{0.35}Dy_{0.01}Fe_{1.64}]BO_{4} |
|     | Sx-B: Fe^{3+}       | 0.438                 | 0.097                | 49.407              | 0.401            | 35.575  |                     |
|     | Sx-B1: Fe^{3+}      | 0.202                 | 0.011                | 48.566              | 0.37             | 46.375  |                     |
|     | Db: Fe^{3+}         | 0.226                 | 0.717                | –                   | 0.399            | 0.752   |                     |
| 0.03| Sx-A: Fe^{3+}       | 0.364                 | 0                  | 52.009              | 0.205            | 17.358  | (Ni_{0.67}Fe_{0.33})_{A} [Ni_{0.33}Dy_{0.01}Fe_{1.61}]BO_{4} |
|     | Sx-B: Fe^{3+}       | 0.455                 | 0.119                | 49.337              | 0.383            | 34.389  |                     |
|     | Sx-B1: Fe^{3+}      | 0.204                 | 0.09                 | 48.55               | 0.38             | 48.253  |                     |
| 0.05| Sx-A: Fe^{3+}       | 0.365                 | 0.008                | 51.941              | 0.257            | 16.783  | (Ni_{0.65}Fe_{0.35})_{A} [Ni_{0.35}Dy_{0.01}Fe_{1.61}]BO_{4} |
|     | Sx-B: Fe^{3+}       | 0.438                 | 0.071                | 49.379              | 0.395            | 35.528  |                     |
|     | Sx-B1: Fe^{3+}      | 0.231                 | –0.018               | 48.559              | 0.402            | 47.689  |                     |
| 0.07| Sx-A: Fe^{3+}       | 0.366                 | –0.008               | 52.057              | 0.242            | 17.866  | (Ni_{0.65}Fe_{0.35})_{A} [Ni_{0.35}Dy_{0.01}Fe_{1.58}]BO_{4} |
|     | Sx-B: Fe^{3+}       | 0.464                 | 0.072                | 49.737              | 0.466            | 25.675  |                     |
|     | Sx-B1: Fe^{3+}      | 0.218                 | –0.023               | 48.76               | 0.422            | 54.952  |                     |
|     | Db: Fe^{3+}         | 0.345                 | 0.625                | –                   | 0.725            | 1.5067  |                     |
| 0.09| Sx-A: Fe^{3+}       | 0.365                 | 0.004                | 52.119              | 0.219            | 19.981  | (Ni_{0.62}Fe_{0.38})_{A} [Ni_{0.38}Dy_{0.01}Fe_{1.55}]BO_{4} |
|     | Sx-B: Fe^{3+}       | 0.424                 | 0.066                | 49.614              | 0.445            | 35.589  |                     |
|     | Sx-B1: Fe^{3+}      | 0.209                 | –0.005               | 48.766              | 0.394            | 45.43   |                     |
| 0.10| Sx-A: Fe^{3+}       | 0.37                  | –0.004               | 52.123              | 0.239            | 20.331  | (Ni_{0.49}Fe_{0.41})_{A} [Ni_{0.49}Dy_{0.01}Fe_{1.55}]BO_{4} |
|     | Sx-B: Fe^{3+}       | 0.441                 | 0.053                | 49.544              | 0.397            | 31.53   |                     |
|     | Sx-B1: Fe^{3+}      | 0.198                 | –0.02                | 48.825              | 0.413            | 46.22   |                     |
|     | Db: Fe^{3+}         | 0.379                 | 0.481                | –                   | 0.696            | 1.9186  |                     |
The achieved relative area for the A and B sites clearly indicated the occupation of Ni$^{3+}$ in the A and B sites. Kumar et al. acknowledged the preferential occupation of Dy$^{3+}$ in the octahedral B sites of Co-ferrites [19,20]. Thus, the cation distribution in the proposed Dy$^{3+}$ substituted nanoferrites was obtained following the formula unit of (Ni$_x$Fe$_{1-y}$)$_A$ (Ni$_{1-y}$Dy$_y$Fe$_{1+y}$)$_B$. The distribution of Fe$^{3+}$ over the A and B sites was observed to be relative to the proportional area of A and B in the Mossbauer sub-spectra. Table 2 summarizes the approximate cation distribution obtained from the Mossbauer spectra. The results in Table 2 revealed that Fe$^{3+}$ cations emigrated from the B site to A site due to Dy$^{3+}$ substitution. The line width of the A site was randomly altered, whereas for B and B$_1$ sites, it was enhanced with the substitution of Fe$^{3+}$ (0.64 Å) in the B sites by Dy$^{3+}$ (0.91 Å) having larger ionic radii than the former one. This observation authenticated the increase in the degree of disorder due to the substitution on B sites.

The values of the hyperfine magnetic fields for the A and B sites (Table 2) in the studied nanosized spinel ferrites were first reduced with an increase in Dy$^{3+}$ contents up to 0.05 and then enhanced at 0.07. Eventually, the hyperfine field for A site was continuously enhanced, but for the B site it was diminished. This alteration in the hyperfine field for the A and B sites was attributed to the addition of the diamagnetic Dy$^{3+}$ that replaced the ferromagnetic Fe$^{3+}$ with a higher magnetic moment (5 $\mu_B$) and lowered the average number of magnetic linkages (Fe$^{3+}$−O−Fe$^{3+}$). Thus, Fe$^{3+}$ nuclei experienced a reduction in the magnetic field at both the sublattices up to the Dy$^{3+}$ content of 0.05. Beyond 0.05, the number of Fe$^{3+}$ at the A site was augmented, thereby increasing the hyperfine magnetic field and magnetic moment of Fe$^{3+}$ at the A site.

### 3.4. ZFC-FC Magnetizations

Figure 5 shows the curves of zero-field-cooled (ZFC) and field-cooled (FC) temperature dependencies of the magnetization, $M_{ZFC}(T)$ and $M_{FC}(T)$, of NiFe$_{2-x}$Dy$_x$O$_4$ (where $x = 0.00, 0.03$ and 0.09) NPs. These measurements were performed in a temperature interval ranging between 2 and 400 K under a DC field of 100 Oe. For $M_{ZFC}(T)$ measurements, the sample was cooled, first of all, from room temperature (RT) to a very low temperature in the absence of an applied field and subsequently the magnetization was recorded by increasing the temperature in the presence of the field. However, in the $M_{FC}(T)$ measurements, the magnetization was recorded by cooling the product in the presence of applied field. A splitting and a large irreversibility between $M_{ZFC}(T)$ and $M_{FC}(T)$ curves for different synthesized products can be clearly seen in Figure 5. The $M_{FC}(T)$ increased gradually and remained constant below temperature $T_s$, while the $M_{ZFC}(T)$ decreased with a lowering of the temperature down to about 4 K. The dispersion of $M_{ZFC}$-$M_{FC}$ versus $T$ curves is congruent with the poly-disperse character of magnetic NPs, with a correlated distribution in particle size and individual anisotropy axes [21]. The enlargement could also owe to dipolar interactions among particles [21].

It is reported in the literature that the manifestation of a peak in the $M_{ZFC}(T)$ plots is associated to the blocking temperature ($T_B$) [22]. The curves of $M_{ZFC}(T)$ of the prepared products showed an incomplete maximum or broad maximum at around the temperature noted $T_B$. This is typical for superparamagnet (SPM) materials, which show the properties of classical paramagnet materials (PM) above $T_B$, where the total spin is equal to the spin of a whole NPs but behave as ferromagnetic (FM) materials below their blocking temperature ($T_B$). Below $T_B$, the $M_{FC}(T)$ and $M_{ZFC}(T)$ curves considerably diverge, and the various ferrite NPs are in the FM state (blocked state). Above $T_B$, the $M_{FC}(T)$ and $M_{ZFC}(T)$ curves coincide, which is because all NPs are in the same SPM state. At $T = T_B$, the thermal activation overcomes the magnetic anisotropy barrier, which leads to fluctuations in magnetization [23]. Therefore, the wide peak at $T_B$ in the $M_{ZFC}(T)$ curves is an indication of a broadened energy barrier distribution. Further, it can be seen that the blocking temperature varies by increasing Dy substitution content. The non-substituted product NiFe$_2$O$_4$ shows a blocking temperature around $T_B \approx 390$ K. The $x = 0.03$ product exhibits a well-defined $T_B$ at around 300 K. By further increasing the amount of Dy, the product synthesized with $x = 0.09$ was not able to reach the $T_B$ within 400 K, so the $T_B$ value is superior than 400 K for $x = 0.09$. It can be seen clearly that the blocking temperature decreases...
for a lower Dy content ($x = 0.03$) and then increases for higher content ($x = 0.09$). The dependence of the $T_B$ on particles size has been reported in previous studies [24]. The lower $T_B$ is attributed to smaller particle size or narrow size distribution. However, the higher $T_B$ represents a larger particle size. Nevertheless, the different $x = 0.00, 0.03$ and 0.09 products show approximately same particles size. Therefore, the variations in blocking temperature with substitution effects are not predominantly influenced by the grain size. Thus, in addition to the particle size effect, the $T_B$ could also be affected by numerous other extrinsic factors, mostly related to interactions among particles and intrinsic factors that principally include a magneto–crystalline, surface and shape anisotropy [22,25]. We noticed in the synthesized product with $x = 0.03$ that the $M_{\text{ZFC}}(T)$ exhibits a breaking at temperatures indicated by the dashed circle in Figure 5.

![Graph](image)

**Figure 5.** $M_{\text{ZFC}}(T)$ and $M_{\text{FC}}(T)$ curves of the three selected NPs.

On the other hand, the $M_{\text{FC}}(T)$ curves increase smoothly for different samples with a decrease of temperature, while a kind of saturation in the magnetization is noticed below the temperature noted by $T_s$ for all samples. It is reported in the literature that for SPM nanoparticles, the curve of $M_{\text{FC}}(T)$ increases continuously [26,27]. Nevertheless, in the case of super-spin glass (SSG) systems in which the interactions among particles are strong, a flat type or a slow increase is observed [26,27].
Therefore, the detected flat nature below $T_s$ in the $M_{\text{FC}}(T)$ curves establishes the occurrence of an SSG-like state. The origin of the observed magnetic features in ZFC-FC magnetization part will be discussed in detail in the analyses of the AC susceptibility measurements. The latter are a useful way to identify the freezing dynamics of the spin-glass (SG) materials.

3.5. AC Susceptibility

For measurements of AC susceptibility ($\chi_{\text{ac}}$), an AC magnetic field ($H_{\text{ac}}$) is applied to the sample and, as a consequence, a resultant magnetic moment is measured. The $\chi_{\text{ac}}$ is represented as follows:

$$\chi_{\text{ac}} = \chi' + i\chi''$$

where $\chi'$ real and $\chi''$ imaginary parts are, respectively, the in-phase and out-phase components of $\chi_{\text{ac}}$. It should be noted that the relaxation time ($\tau$) of the AC susceptibility measurement is not based upon the energy barrier ($E_a = K_{\text{eff}}V$ where $K_{\text{eff}}$ is the effective anisotropy constant and $V$ is the volume of particles). However, it is influenced by the external excitation frequency. The AC susceptibility measurements give important details about the dynamics of the systems and the strength of exchange interactions between the magnetic nano-particles (MNPs) and between the different cations.

Firstly, we will discuss the $\chi'$ real part measurements of the two NPs samples with $x = 0.00$ and 0.03. Figure 6 presents the curves of $\chi'$ versus $T$, ranging from 350 to 2 K, for $x = 0.00$ and 0.03 products, performed in the presence of an $H_{\text{ac}} = 10$ Oe and in a frequency range of $50 - 10^4$ Hz. The magnitude of $\chi'$ for $x = 0.03$ increased slightly compared to the non-substituted product ($x = 0.00$), which is in accordance with $M_{\text{ZFC}}(T)$ and $M_{\text{FC}}(T)$ measurements. The in-phase AC susceptibility data of the different samples showed dispersion and a decrease in magnitude while increasing the applied frequency from 50 Hz to 10 kHz. The $\chi'(T)$ curve of the non-substituted NiFe$_2$O$_4$ NPs exhibited a peak at around 300 K. However, the $x = 0.03$ product did not show any peak up to 350 K.

![Figure 6. $\chi'(T)$ curves of the prepared (a) NiFe$_2$O$_4$ and (b) NiFe$_{1.97}$Dy$_{0.03}$O$_4$ NPs.](image-url)
Figure 7 shows the $\chi''(T)$ curves for NiFe$_{2-x}$Dy$_x$O$_4$ (where $x = 0.00$ and $0.03$) performed in a $H_{ac} = 10$ Oe and in the frequency range of $50$–$10^4$ Hz. It can be seen that both samples display two peaks—the first at the higher temperature indicated by $T_B$ in the figure, which is associated with magnetic blocking of huge core spins, and the second indicated by $T_s$, which can be associated with the spin-glass freezing on the surface of a single NP [28]. The $\chi'(T)$ curves do not offer any information about these two peaks, hence from now on we will focus only on analyses of $\chi''(T)$ curves.

At the same applied frequency, the $T_B$ and $T_s$ shifted to lower temperatures with Dy substitution compared to the non-substituted one. This is consistent with the M$_{ZFC}$ analyses. Both the blocking temperature $T_B$ and spin-glass freezing temperature $T_s$ are affected by frequency. Both show a shift to higher temperatures upon increasing the value of the applied frequency ($f$). Similar behavior is observed in the spin-frustrated system of CoFe$_2$O$_4$ NPs dispersed in an SiO$_2$ matrix [28]. The shifting with $f$ is helpful for evaluating dynamic magnetic behaviors, deducing the anisotropic energy, the magnetic anisotropy, and the interaction strength between MNPs.

Various physical laws can be used to investigate the $f$-dependence shift of $T_B$ and $T_s$ temperatures. The Neel–Arrhenius (N–A) law was first tested to fit the experimental data (Figure 8). This theory is valid for thermal excitations of non-interacting single-barrier NPs and is expressed as follows [29,30]:

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right)$$

where $\tau = 1/f$ is the measured time, $\tau_0$ is the jump attempt time (in the range of $10^{-9}$–$10^{-13}$ s), $k_B$ is the Boltzmann constant, and $E_a = K_{eff}V$ is the activation energy barrier. The estimated values of $\tau_0 = 1/f_0$, $E_a/k_B$ and $K_{eff}$ for different samples are given in Table 3. The best N–A fit offers very
unreasonable values for \( \tau_0 \) and \( E_a/k_B \). This indicates that the synthesized products do not obey the thermally activated N–A law and, as a consequence, they are non-interacting.

The Vogel–Fulcher (V–F) law is a useful model for investigating the interactions between NPs. This law uses an additional parameter, \( T_0 \), that represents the strength of inter-particle interactions. Based on this model, the relaxation is described as follows \cite{29,30}:

\[
\tau = \tau_0 \exp\left(\frac{E_a}{k_B(T - T_0)}\right).
\]

![Figure 8](image_url) Plots of (a) \( \ln(f) \) versus \( 1/T_B \) and (b) \( \ln(f) \) versus \( 1/T_s \) for two selected NiFe\(_{2-x}\)Dy\(_x\)O\(_4\) NPs where \( x = 0.00 \) and \( 0.03 \) fit to the Neel–Arrhenius (N–A law) (solid lines).

**Table 3.** Fitting parameters (\( \tau_0, E_0/k_B \) and \( K_{\text{eff}} \)) of prepared NiFe\(_{2-x}\)Dy\(_x\)O\(_4\) (\( x = 0.00 \) and \( 0.03 \)) NPs estimated using different laws.

| Models         | Parameters | Values                     |
|----------------|------------|----------------------------|
| Neel–Arrhenius | \( \tau_0 (s) \) | \( 1.05 \times 10^{-70} \) \( 1.68 \times 10^{-32} \) \( 1.69 \times 10^{-16} \) \( 1.26 \times 10^{-392} \) |
| \( E_0/k_B (K) \) | \( 49,083 \) \( 17,403 \) 2150 184,793 |
| \( K_{\text{eff}} \) (erg/cm\(^3\)) | \( 3.09 \times 10^5 \) \( 1.09 \times 10^5 \) \( 1.35 \times 10^4 \) \( 1.16 \times 10^6 \) |
| Vogel–Fulcher  | \( \tau_0 (s) \) | \( 5.45 \times 10^{-10} \) \( 1.32 \times 10^{-9} \) \( 8.00 \times 10^{-7} \) \( 6.06 \times 10^{-46} \) |
| \( E_0/k_B (K) \) | \( 367.57 \) \( 621.53 \) 100.38 2188.95 |
| \( T_0 (K) \) | \( 292.71 \) \( 216.76 \) 58.82 183.84 |
| \( K_{\text{eff}} \) (erg/cm\(^3\)) | \( 2.32 \times 10^3 \) \( 3.92 \times 10^3 \) \( 6.34 \times 10^2 \) \( 1.38 \times 10^4 \) |
| Critical slowing down | \( \tau_0 (s) \) | **** *** 2.88 \( \times 10^{-9} \) 2.50 \( \times 10^{-12} \) |
| \( T \) (K) | **** **** 58.39 205.55 |
| \( z \) | **** **** 5.77 3.95 |
The fitting data using the V–F law of the plots of $f$ vs. $T_B$ and $f$ vs. $T_s$ for the prepared products are illustrated in Figure 9a,b, respectively. The different estimated parameters are summarized in Table 3. The analysis of $f$-dependent $T_B$ now gives reasonable $\tau_0$ and $E_a/k_B$ values. Obviously, the $T_0$ values are not negligible compared to $T_B$. The occurrence of $T_0$ confirms the presence of moderate inter-particle interactions between the NPs [28–30]. It is found, moreover, that $\tau_0$ increased more for the $x = 0.03$ product than for the $x = 0.00$ one. The increase in the $\tau_0$ for $x = 0.03$ product suggests the strengthening of interactions between NPs [29,30]. Compared to the $x = 0.00$ product, the values of $E_a/k_B$ and $K_{eff}$ improved with Dy substitution for $x = 0.03$. This improvement resulted from the strengthening of magnetic interactions among different NPs and the increase of magnetic anisotropy sources [29,30].

Figure 9. Plots of (a) $f$ versus $T_B$ and (b) $f$ versus $T_s$ for NiFe$_{2-x}$Dy$_x$O$_4$ ($x = 0.00$ and $0.03$) NPs (solid lines present the Vogel–Fulcher (V–F) fit).

In other hand, the investigation of $f$ vs. $T_s$ provides unphysical values for $\tau_0$. Therefore, the critical slowing down (CSD) law is used to study the presence of SG behavior in the synthesized NPs. Based on this model, the relaxation is expressed as [30]:

$$
\tau = \tau^*_0 \left( \frac{T_s}{T_g} - 1 \right)^{-(2\nu)}
$$

where $\tau^*_0$ is associated to the coherence time of coupled individual “atomic” spins in the NP (in the range $10^{-6}$–$10^{-13}$ s) [31], $T_g$ is the SG freezing temperature, and $T_s$ is the $f$-dependent freezing temperature. The “$2\nu$” is the critical exponent that offers information about the SG, and it varies from 4 to 12 for various SG systems [28]. We fit the same $f$ vs. $T_s$ data using the CSD law, in order to examine the possibility of the SG nature (Figure 10). The various deduced parameters are listed in Table 3. The obtained reasonable values of $\tau_0$, $T_g$ and “$2\nu$” proved the existence of SG behavior in the prepared samples. Similar comportment has been reported in numerous products, such as CoFe$_2$O$_4$/(SiO$_2$)$_x$ systems [28], Fe$_3$O$_4$ MNPs ($\nu = 8.2$ and $\tau \sim 10^{-9}$ s) [32,33], soft ferrite Ni$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ NPs ($\nu = 8.01$...
and $\tau \sim 10^{-12}$ s) [34], and La$_{0.9}$Sn$_{0.1}$MnO$_3$ NPs [35]. It is reported that the strength of magnetic interactions increases based on the decreasing “$zv$” exponent. The non-substituted NiFe$_2$O$_4$ product exhibits a “$zv$” value equal to 5.11, and it decreases to 3.95 with Dy substitution for $x = 0.03$. This result indicates the improvement of the magnetic interactions among NPs for the $x = 0.03$ product.

![Figure 10. Plots of $f$ versus $T_s$ for the two selected $x = 0.00$ and 0.03 NPs. The solid lines represent the critical slowing down (CSD) fit.](image)

4. Conclusions

Series of Dy$^{3+}$ doped ferrite nanoparticles of NiFe$_{2-x}$Dy$_x$O$_4$ ($0.0 \leq x \leq 0.1$) NPs were prepared using a hydrothermal method. The as-prepared specimens were thoroughly characterized using various analytical measurement techniques to determine their structure, morphology, and distinct magnetic traits. An XRD pattern of nanoferrites confirmed the formation of a spinel cubic structure. The Mössbauer spectra displayed the cation distribution, verifying the occupation of Dy$^{3+}$ ions at octahedral B sites. The measurements of ZFC-FC magnetization and AC susceptibility were examined. The magnetic data showed the existence of two critical temperatures. The first one is the blocking temperature $T_B$, which corresponds to the magnetic blocking of huge core spins, and the second is $T_s$, which can be associated to spin-glass freezing arising on the surface of a single NP. The $T_B$ and $T_s$ temperatures vary with the Dy substitution. This is due to numerous intrinsic and extrinsic factors that principally include magneto-crystalline factors, interactions among particles, surface, and shape anisotropy. Furthermore, both the $T_B$ and $T_s$ temperatures are affected by applied frequency. Various physical laws, such as Neel-Arrhenius, Vogel-Fulcher, and critical slowing down, are used to investigate the $f$-dependence shift of the $T_B$ and $T_s$ temperatures. It was found that the Dy substitution enhances the magnetic interactions. Compared to the $x = 0.00$ product, the $E_s/k_B$ and $K_{eff}$ values improved for $x = 0.03$. This proved that the magnetic interactions are enhanced due to the Dy substitution.

**Author Contributions:** Synthesis of the sample (M.A.A., Y.S. and A.B.). XRD investigation and analysis (M.A.A. and A.B.). Investigation and writing of the ZFC-FC magnetization and AC susceptibility (Y.S.). Investigation and analysis of the Mossbauer spectra (H.G.). Participation in drafting the article or revising it critically for important intellectual content (S.A., A.M., I.E. and A.V.T). Supervision, review, and editing (M.A.A., Y.S. and A.B.).

**Funding:** The authors highly acknowledge the Institute for Research & Medical Consultations (Projects application No. 2017-IRMC-S-3; No. 2018-IRMC-S-1 and No. 2018-IRMC-S-2) and the Deanship for Scientific Research (Projects application No. 2017-576-IRMC and No. 2018-209-IRMC) of Imam Abdulrahman Bin Faisal University (Saudi Arabia) for supporting this study.
Acknowledgments: The authors thank the Institute for Research & Medical Consultations (IRMC) of Imam Abdulrahman Bin Faisal University (IAU—Saudi Arabia) for the supports. The technical assistance provided by Core Labs of King Abdullah University of Science and Technology (KAUST) is highly appreciated.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kavas, H.; Kasapoğlu, N.; Baykal, A.; Köseoğlu, Y. Characterization of NiFe2O4 nanoparticles synthesized by various methods. Chem. Pap. 2009, 63, 450–455. [CrossRef]

2. Ati, A.A.; Othaman, Z.; Samavati, A. Influence of cobalt on structural and magnetic properties of nickel ferrite nanoparticles. J. Mol. Struct. 2013, 1052, 177–182. [CrossRef]

3. Vigneswari, T.; Raji, P. Structural and magnetic properties of calcium doped nickel ferrite nanoparticles by co-precipitation method. J. Mol. Struct. 2017, 1127, 515–521. [CrossRef]

4. Wahba, A.M.; Mohamed, M.B. Structural, magnetic, and dielectric properties of nanocrystalline Cr-substituted Co0.3Ni0.7Fe2O4 ferrite. Ceram. Int. 2014, 40, 6127–6135. [CrossRef]

5. Sözeri, H.; Alvero˘ glu, E.; Kurtan, U.; Şenel, M.; Baykal, A. Cobalt substituted nickel ferrites via Pechini’s sol–gel citrate route: X-band electromagnetic characterization. J. Supercond. Nov. Magn. 2013, 26, 213–218.

6. Mozaﬁari, M.; Amighian, J.; Darsheshdar, E. Magnetic and structural studies of nickel-substituted cobalt ferrite nanoparticles, synthesized by the sol–gel method. J. Magn. Magn. Mater. 2014, 350, 19–22. [CrossRef]

7. Yaseneva, P.; Bowker, M.; Hutchings, G. Structural and magnetic properties of Zn-substituted cobalt ferrites prepared by co-precipitation method. Phys. Chem. Chem. Phys. 2011, 13, 18609. [CrossRef] [PubMed]

8. Srinivasasumurthy, K.; Angadi, V.; Kubrin, S.; Mattepanavar, S.; Kumar, P.M.; Rudraswamy, B. Evidence of enhanced ferromagnetic nature and hyperfine interaction studies of Ce-Sm doped Co-Ni ferrite nanoparticles for microphone applications. Ceram. Int. 2018, 44, 18878–18885. [CrossRef]

9. Stergiou, C. Magnetic, dielectric and microwave absorption properties of rare earth doped Ni–Co and Ni–Co–Zn spinel ferrites. J. Magn. Magn. Mater. 2017, 426, 629–635. [CrossRef]

10. Boda, N.; Boda, G.; Naidu, K.C.B.; Srinivas, M.; Batoo, K.M.; Ravinder, D.; Reddy, A.P. Effect of rare earth elements on low temperature magnetic properties of Ni and Co-ferrite nanoparticles. J. Magn. Magn. Mater. 2019, 473, 228–235. [CrossRef]

11. Singh, R.K.; Shah, J.; Kotnala, R. Magnetic and dielectric properties of rare earth substituted Ni0.5Zn0.5Fe1.95O0.05O4 (R = Pr, Sm and La) ferrite nanoparticles. Mater. Sci. Eng. B 2016, 210, 64–69. [CrossRef]

12. Akhtar, M.N.; Khan, M.A. Effect of rare earth doping on the structural and magnetic features of nanocrystalline spinel ferrites prepared via sol gel route. J. Magn. Magn. Mater. 2018, 460, 268–277. [CrossRef]

13. Sahariya, J.; Mund, H.S.; Sharma, A.; Dashora, A.; Itou, M.; Sakurai, Y.; Ahuja, B.L. Magnetic properties of NiFe2−xRe2xO4 (RE=Dy, Gd) using magnetic Compton scattering. J. Magn. Magn. Mater. 2014, 360, 113–117. [CrossRef]

14. Bhattacharyya, M.; Noor-A-Alam, M.; Vemuri, R.; Ramana, C.V. Correlation between microstructure, electrical and optical properties of nanocrystalline NiFe1.925 Dy0.075 O4 thin films. RSC Adv. 2012, 2, 941–948. [CrossRef]

15. Almessiere, M.; Slimani, Y.; Güner, S.; Baykal, A.; Erkan, I. Effect of dysprosium substitution on magnetic and structural properties of NiFe2O4 nanoparticles. J. Rare Earths 2019. [CrossRef]

16. Chawla, S.K.; Meena, S.S.; Kaur, P.; Mudassainiyan, R.K.; Yusuf, S.M. Effect of site preferences on structural and magnetic switching Properties of Co–Zr doped strontium hexaferrite SrCo2(12−2x)ZrO19. J. Magn. Magn. Mater. 2015, 378, 84–91. [CrossRef]

17. Josephyus, R.J.; Narayanasamy, A.; Shinoda, K.; Jeyadevan, B.; Tohji, K. Synthesis and magnetic properties of the size-controlled Mn–Zn ferrite nanoparticles by oxidation method. J. Phys. Chem. Solids 2006, 67, 1510–1517. [CrossRef]

18. Chae, K.P.; Kwon, W.H.; Lee, J.-G. Influence of aluminum doping in Li–Co–Ti ferrite. J. Magn. Magn. Mater. 2012, 324, 2701–2705. [CrossRef]

19. Kumar, H.; Sing, J.P.; Srivastava, R.C.; Patel, K.R.; Chae, K.H. Synthesis and characterization of Dy3CoFe2−xO4 nanoparticles. Superlattices Microstruct. 2017, 109, 296–306. [CrossRef]
20. Kumar, H.; Srivastava, R.; Singh, J.P.; Negi, P.; Agrawal, H.; Das, D.; Chae, K.H. Structural and magnetic study of dysprosium substituted cobalt ferrite nanoparticles. *J. Magn. Magn. Mater.* 2016, **401**, 16–21. [CrossRef]

21. Morales, M.-B.; Phan, M.-H.; Pal, S.; Frey, N.-A.; Srikanth, H. Particle blocking and carrier fluid freezing effects on the magnetic properties of Fe$_3$O$_4$-based ferrofluids. *J. Appl. Phys.* 2009, **105**, 07B511. [CrossRef]

22. Humbe, A.V.; Kounsalye, J.S.; Shisode, M.V.; Jadhav, K. Rietveld refinement, morphology and superparamagnetism of nanocrystalline Ni$_{0.70-x}$Cu$_x$Zn$_{0.30}$Fe$_2$O$_4$ spinel ferrite. *Ceram. Int.* 2018, **44**, 5466–5472. [CrossRef]

23. Graham, C.D. *Introduction to Magnetic Materials*; Wiley: Hoboken, NJ, USA, 2009.

24. Bhowmik, R.; Aneeshkumar, K. Low temperature ferromagnetic properties, magnetic field induced spin order and random spin freezing effect in Ni$_{1.5}$Fe$_{1.5}$O$_4$ ferrite; prepared at different pH values and annealing temperatures. *J. Magn. Magn. Mater.* 2018, **460**, 177–187. [CrossRef]

25. Ajroudi, L.; Mliki, N.; Bessais, L.; Madigou, V.; Villain, S.; Leroux, C.; Leroux, C. Magnetic, electric and thermal properties of cobalt ferrite nanoparticles. *Mater. Res. Bull.* 2014, **59**, 49–58. [CrossRef]

26. Peddis, D.; Cannas, C.; Piccaluga, G.; Agostinelli, E.; Fiorani, D. Surface spin freezing effects on enhanced saturation magnetization and magnetic anisotropy in CoFe$_2$O$_4$ nanoparticles. *Nanotechnology* 2010, **21**, 125705. [CrossRef]

27. Chen, X.; Bedanta, S.; Petracic, O.; Kleemann, W.; Sahoo, S.; Cardoso, S.; Freitas, P.P.; Freitas, P. Superparamagnetism versus superspin glass behavior in dilute magnetic nanoparticle systems. *Physica B* 2005, **72**, 214436. [CrossRef]

28. Zeb, F.; Sarwer, W.; Nadeem, K.; Kamran, M.; Mumtaz, M.; Krenn, H.; Letofsky-Papst, I. Surface spin-glass in cobalt ferrite nanoparticles dispersed in silica matrix. *J. Magn. Magn. Mater.* 2016, **407**, 241–246. [CrossRef]

29. Almessiere, M.A.; Slimani, Y.; Gungune¸s, H.; Baykal, A.; Trukhanov, S.V.; Trukhanov, A.V. Manganese/Yttrium Codoped Strontium Nanohexaferrites: Evaluation of Magnetic Susceptibility and Mossbauer Spectra. *Nanomaterials* 2019, **9**, 24. [CrossRef]

30. Slimani, Y.; Almessiere, M.; Baykal, A. AC susceptibility study of Cu substituted BaFe$_{12}$O$_{19}$ nanohexaferrites. *Ceram. Int.* 2018, **44**, 13097–13105. [CrossRef]

31. Kumar, D.; Banerjee, A. A critical examination of magnetic states of La$_{0.5}$Ba$_{0.5}$CoO$_3$: Non-Griffiths phase and interacting ferromagnetic-clusters. *arXiv* 2012, arXiv:1211.4936.

32. Suzuki, M.; Fullem, S.I.; Suzuki, I.S.; Wang, L.; Zhong, C.-J. Observation of superspin-glass behavior inFe$_3$O$_4$nanoparticles. *Phys. B* 2009, **79**, 024418. [CrossRef]

33. Fiorani, D.; Testa, A.M.; Lucari, F.; D’Orazio, F.; Romero, H. Magnetic properties of maghemite nanoparticle systems: Surface spin and interparticle interaction effects. *B: Condens. Matter* 2002, **320**, 122–126. [CrossRef]

34. Rahimi, M.; Kameli, P.; Ranjbar, M.; Salamati, H. The effect of polyvinyl alcohol (PVA) coating on structural, magnetic properties and spin dynamics of Ni$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ ferrite nanoparticles. *J. Magn. Magn. Mater.* 2013, **347**, 139–145. [CrossRef]

35. Eshraghi, M.; Kameli, P. Structural and Magnetic Properties of La0.9Sr0.1MnO3 Micro and Nanometer-Sized Manganite Samples. *J. Mater. Sci.* 2014, **3**, 1.