Magnetic Properties of Lithium Ferrite Nanoparticles with a Core/Shell Structure

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Abstract: We present a magnetic study of lithium ferrite nanoparticles of composition Li0.5Fe2.5O4 synthesized by a citrate gel decomposition method. The as prepared sample was composed of nearly spherical nanoparticles with an average particle size <d> ~ 12 nm. Further annealing at 573 K and 673 K for 4 hours did not increase particle size noticeably, while annealing at 973 K led to morphology changes and significant increase in size ranging from 40 to above 200 nm. The magnetic properties of samples have been studied using Mössbauer spectroscopy, and static magnetic measurements. The hyperfine parameters obtained from Mössbauer data at T = 10 K are in agreement to the bulk lithium ferrite phase. Annealed samples showed an evolution from monodomain structure to polycrystalline behaviour, what is evident from TEM images, as well as the evolution of the coercive filed, Hc, and the saturation magnetization, Ms, with particle size increase. The exchange interactions have been observed in the single–domain nanoparticles, which probably originate from their core–shell structure. At low temperatures and in high enough magnetic fields, the cubic magnetic anisotropy stays preserved and the magnetic moments in the particle core are aligned along (111) directions of the spinel structure.

Keywords: Anisotropy, ferrites, nanostructured materials, magnetic measurements, Mössbauer spectroscopy, oxide materials.

1. INTRODUCTION

Lithium ferrite (Li0.5Fe2.5O4) has been a widely investigated material due to its importance in construction and engineering of many electromagnetic and microwave devices [1-3]. This material crystallizes in the spinel crystal structure, AB2O4, where A and B denote lattice sites tetrahedrally and octahedrally coordinated by oxygen ions, respectively [4, 5]. Bulk lithium ferrite has an inverse cation distribution of the form (Fe3+)A[Li0.5 Fe1.5]B. The interplay between superexchange interactions of Fe3+ ions at A and B sublattices gives rise to ferrimagnetic ordering of magnetic moments, with a high Curie–Weiss temperature (ΘCW ~ 900 K), and a saturation magnetization (Ms(bulk) ~ 68.7 Am2/kg, at room temperature) [6, 7].

The magnetic anisotropy of this material is a key parameter that determines the overall magnetic behaviour, through the effective anisotropy constant Keff [8]. In bulk materials, the main contribution to the Keff arises from the magnetocrystalline anisotropy represented by the first–order magnetocrystalline anisotropy constant, K1. This anisotropy is determined by the strength of the L–S coupling and, therefore, it is affected by the electron configuration of the Fe3+ ions. In bulk lithium ferrite, the high spin configuration of Fe3+ ions (3d7) makes the contribution of the orbital magnetic moment negligible, and therefore a low magnetocrystalline anisotropy is expected for this material [9]. Due to the low magnetocrystalline anisotropy and magnetostriiction values (i.e. the low magnetic losses), this ferrite is commonly used in microwave devices [3].

By decreasing particle size to the nanoscale, the magnetic behavior of material can be significantly different from the bulk counterpart. The main origin of these differences is due to the finite size and surface effects, usually influenced by the presence of interparticle interactions (exchange and/or dipolar) [10-12]. Magnetic behavior of nanoparticles (NPs) is commonly explained within the frame of a single energy–barrier model, where the flipping of magnetic moments is connected with overcoming the energy potential represented by E = KeffV (V is the average nanoparticle volume). For magnetic nanoparticles, the value of an effective anisotropy constant, Keff, is determined not only by the contribution of the bulk (magnetocrystalline) anisotropy, but also by the surface, strain and/or shape anisotropy, as well as the anisotropy arising from interparticle interactions [12-14]. Magnetic nanoparticles are single–domain below a critical particle size, that depends on the effective magnetic anisotropy. For lithium ferrite NPs, the critical size is still a matter of discussion [4]. Single domain NPs show superparamagnetic behavior above a certain temperature known as the blocking temperature, T B. In the superparamagnetic state, the thermal energy, kBT, can overcome energy barrier, ΔE, and allows freely flipping of single spins between the easy directions of magnetization. The situation becomes more difficult in the presence of moderate–to–strong interparticle interactions, when the collective magnetic behavior and an increase of the blocking temperature are observed [15].

Previous works on bulk lithium ferrite revealed the cubic magnetic anisotropy in this spinel [3, 16]. In the presence of external magnetic field, magnetic moments direct along (111) crystallographic directions (easy axes of magnetization), while (100) directions determine hard axes of magnetization [16]. In spinel compounds, the octahedral (B) sites produce anisotropy that favors the (111) axes (easy directions). According to G.F. Dionne, in most cases, the first–order magnetocrystalline anisotropy constant, K1, is determined by the octahedral (B) site contributions, while the contributions of the tetrahedral (A) sites are opposite in sign and significantly smaller [3]. On the contrary, Z.C. Xu [17], revealed that in Li0.5Fe2.5O4 the K1 value depends mainly on the contribution of Fe3+ ions in A sites. Nevertheless, negative values of K1 have been found in both cases. V.J. Folen considered the temperature dependence of K1 value in ordered (α–; space group P43m) and disordered (β–; S.G. Fd-3m) phase of Li0.5Fe2.5O4 single crystal [18]. He found that the absolute magnitude of K1 increases with temperature decrease down to 77 K, but below 77 K no further changes in the magnitude of K1 constant have been observed. Also, he revealed that disordered, β–phase of lithium ferrite single crystal possesses the higher absolute magnitude of K1 in the temperature range from 77 K to 300 K.

In this study, we have investigated the magnetic behavior of an assembly of lithium ferrite NPs, prepared by citrate gel decomposition method, using Mössbauer spectroscopy and the static magnetization measurements. The special focus has been put on the effective magnetic anisotropy analysis. In our previous work [19], we
studied in detail the evolution of structural and microstructural parameters of lithium ferrite nanopowder with annealing.

2. MATERIALS AND METHODS

The lithium ferrite phase (Li$_0.5$Fe$_{2.5}$O$_4$) was synthesized by a citrate gel decomposition method. Aqueous solutions of LiNO$_3$ and Fe(NO$_3$)$_3$·9H$_2$O were mixed with 5 mol % of Li ions in excess comparing the required stoichiometry in order to avoid formation of imperity (usually hematite) [20]. Then, the citric acid was added into a mixture of metal nitrates and the resulting solution was stirred and dried at 353 K for 12 hours. After cooling down to room temperature a dried gel was sintered at 453 K for 12 hours [19]. The as prepared sample (labeled S1 hereafter) was further annealed at 573 K (sample S2), 673 K (sample S3), and 973 K (sample S4) for 4 hours to follow the magnetic and structural evolution towards the bulk–like behavior. The morphology of the samples was studied by transmission electron microscopy (TEM) using JEOL JEM 2100 HR microscope operated at 200 kV, while high-resolution TEM (HRTEM) images were recorded on a FEI TECNAI G2 30F microscope operated at 300 kV.

The magnetic properties of all samples were studied with a commercial superconducting quantum interferometer (SQUID) magnetometer (Quantum Design, MPMS-5S). Magnetization and susceptibility were measured as a function of temperature and magnetic field. Zero-field cooled (ZFC) and field-cooled (FC) curves were recorded in the temperature range 2–350 K, in cooling magnetic field $H_{\text{fc}} = 7.96$ kA/m, for all samples, and additionally for sample S3 in a field of 39.79 kA/m. Hysteresis loops, $M(H)$, of all samples were collected at 5 K, in magnetic field up to 3.98 MA/m, while for sample S1 the hysteresis loop was additionally recorded in field-cooled mode by cooling the sample from room temperature to $T = 5$ K in the presence of magnetic field of 3.98 MA/m.

$^{57}$Fe Mössbauer spectra of samples S1, S3 and S4 were collected at $T = 10$ K in the transmission geometry, using a $^{57}$Co(Rh) source. Experimental data were fitted to Lorentzian lineshape using a least square based method. The isomer shifts values were calculated relative to the center of α–Fe foil spectrum recorded at room temperature.

3. RESULTS AND DISCUSSIONS

It has recently been shown that by a citrate gel decomposition method it is possible to obtain pure lithium ferrite nanoparticles, better crystallized comparing to other synthesis routes (e.g. Pechini method) [20, 21]. Concerning structural and microstructural characteristics of such produced Li$_0.5$Fe$_{2.5}$O$_4$ nanoparticles, the TEM and XRD analysis showed that annealing up to 673 K did not induce significant changes, neither on the average particle size (Fig. 1) nor on the cations distribution (in samples S1–S3) [19]. The average particle diameter, $<d>$, obtained from TEM analysis is around 12 nm for the as prepared sample S1. Further annealing at 973 K (sample S4) induced significant changes in morphology, particle size and cations distribution. The particle size distribution became bimodal, and small particles of about 40–90 nm in size could be noticed altogether with bigger ones of irregular shape with size $>100$ nm. In our previous work [19] was shown that inverse spinel structure stay preserved in all nanocrystalline Li$_0.5$Fe$_{2.5}$O$_4$ (tetrahedral (A) sites are completely occupied by Fe$^{3+}$ ions). A partial ordering of Li$^{+}$ and Fe$^{3+}$ ions inside octahedral (B) sublattice has been found in samples annealed up to 673 K (S.G. P4$_3$2c), with the cation distribution which can be represented, on average, by formula: (Fe$^{3+}$)$_{0.8}$(Li$^{+}$.Fe$^{3+}$)$_{0.2}$(Li$^{+}$)$^{1.3}$Fe$^{3+}$$_{1.2}$. Annealing at 973 K induces full ordering of Li$^{+}$ and Fe$^{3+}$ ions at the B sites of the spinel lattice, with the cation distribution (Fe$^{3+}$)$_{1.3}$(Li$^{+}$.0.5)ab (Fe$^{3+}$.1.5)cd [19]. Since, the occupancy ratio of Fe$^{3+}$ ions at the A and B sites stay unchanged with sample annealing, it is expected that the strong superexchange interactions between Fe$^{3+}$ ions at the A and B sites, $J_{ab}$, can give rise to the high magnetization of nanocrystalline lithium ferrite particles.

3.1. The Mössbauer Spectra Analysis

The low-temperature Mössbauer spectra of samples S1, S3 and S4 are shown in (Fig. 2). The spectrum of the as prepared sample S1 could be fitted with three sextets, two of them, with hyperfine fields value of $B_{\text{hf}} = 51.4$ T and 53.3 T, correspond to Fe$^{3+}$ in A and B sites in the spinel lattice, respectively. A third sextet, amounting a 19.7 % of the total spectral area, displayed lower hyperfine field of $B_{\text{hf}} = 48.2$ T, assigned to Fe ions at the disordered surface of the NPs. According to the above interpretation, the Mössbauer spectra of samples S3 and S4 could be fitted with the two sextets from A and B sites of the bulk spinel structure, without the presence of the signal from the disordered surface. The values of the fitted hyperfine parameters are summarized in Table 1. All the fitted hyperfine field values assigned to Fe$^{3+}$ in A and B sites showed only slight variation after annealing (51.4 T $< B_{\text{hf}}(A) < 51.9$ T; 53.3 T $< B_{\text{hf}}(B) < 53.8$ T). These values are in agreement with previously reported data for lithium ferrite [16, 22–24]. Specifically, for nanocrystalline Li$_0.5$Fe$_{2.5}$O$_4$ the typical values of hyperfine fields $B_{\text{hf}}(A)$ and $B_{\text{hf}}(B)$, measured at low temperatures, lay between the 51.0–51.8 T and 52.0–53.6 T, respectively [16, 22]. The presence of a third magnetic component found in the as prepared sample could originate from chemically and magnetically disordered surface layer. Based on the results of crystal structure analysis [19], a non-uniform distribution of Li$^{+}$ ions might be expected across the particles diameter in nanocrystalline lithium ferrite, with possible accumulation of Li$^{+}$ ions at the surface of NPs. Apart from the surface spin disordering, the presence of Li$^{+}$ ions in excess can give rise to decrease of hyperfine interaction between Fe$^{3+}$ ions. It could be a reason of appearance of the third magnetic component in Mössbauer spectra of the as prepared sample. It is worth to notice that in all samples the difference between isomer shifts for A and B sites, $I_{S_A} - I_{S_B}$, is very close to the value 0.08 mm/s which is characteristic for bulk lithium ferrite sample [25]. Hence, by Mössbauer spectroscopy it is confirm appearance of pure lithium ferrite phase in samples.

3.2. DC Magnetization Study

The magnetic behavior of lithium ferrite NPs was analyzed from the temperature dependence of the magnetization measured in zero–field–cooled and field–cooled (ZFC–FC) modes (Fig. 3a). Divergency of ZFC and FC magnetization is found in all samples, in the whole range of measured temperatures (from 2 K to 350 K). In samples S1, S2 and S3, FC magnetization, $M_{\text{FC}}$, slightly increases with temperature decrease and tends to a constant value at temperatures below 100 K, while for sample S4, $M_{\text{FC}}$ is almost constant in this temperature range. Only in the sample S1, the ZFC magnetization curve, $M_{\text{ZFC}}(T)$, shows a very broad and pronounced maximum at $T_{\text{max}} \approx 240$ K, while in samples S2–S4 a constant increase of $M_{\text{ZFC}}$ with temperature increases is observed. The ZFC–FC magnetization of sample S3 have also been measured at DC magnetic fields of 39.79 kA/m (Fig. 3b), and the maximum in $M_{\text{ZFC}}$ curve was found at $T_{\text{max}} \approx 265$ K. The great discrepancy noticed between all $M_{\text{ZFC}}$ and $M_{\text{FC}}$ curves indicate either a superparamagnetic or a glassy behavior. The flattening of FC curve at lower temperature can be an indication of the interparticle interactions, which additionally shift $T_{\text{max}}$ towards higher value. A broad maximum in ZFC curve indicates a wide distribution of the blocking temperatures, $T_{B}$.

Magnetization as a function of magnetic field, $M(H)$, measured at 5 K, are depicted at (Fig. 4). Typical hysteresis behavior is detected in all samples. The samples S1–S3 have very similar the coercivity, $H_{C}$, of about 31.8 kA/m, while with increasing the average particle size (sample S4), this value becomes lower and amounts 19.8 kA/m (see Table 2). The same observation could be
Fig. (1). Left: TEM images of samples S1, S3 and S4; right: particle size distribution of samples S1 and S4, and HRTEM image of sample S3.

Table 1. The Mössbauer Parameters: $IS$ – Isomer Shift; $\epsilon$ – Quadrupolar Splitting, $B_{hf}$ – Hyperfine Field, $\Gamma$ – Linewidth, and Spectral Area (%), Obtained from the Fit of Mössbauer Spectra of Samples S1, S3 and S4, Collected at 10 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component</th>
<th>$IS$ (mm/s)</th>
<th>$\epsilon$ (mm/s)</th>
<th>$B_{hf}$ (T)</th>
<th>$\Gamma$ (mm/s)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>A</td>
<td>0.41</td>
<td>0.001</td>
<td>51.4</td>
<td>0.23</td>
<td>40.5</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.46</td>
<td>0.014</td>
<td>53.3</td>
<td>0.20</td>
<td>39.5</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.47</td>
<td>-0.012</td>
<td>48.2</td>
<td>0.32</td>
<td>19.7</td>
</tr>
<tr>
<td>S3</td>
<td>A</td>
<td>0.39</td>
<td>-0.004</td>
<td>51.5</td>
<td>0.26</td>
<td>55.6</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.46</td>
<td>0.014</td>
<td>53.5</td>
<td>0.19</td>
<td>44.3</td>
</tr>
<tr>
<td>S4</td>
<td>A</td>
<td>0.36</td>
<td>-0.007</td>
<td>51.9</td>
<td>0.27</td>
<td>42.5</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.45</td>
<td>0.010</td>
<td>53.8</td>
<td>0.25</td>
<td>57.5</td>
</tr>
</tbody>
</table>
found in literature [2, 13]. For particles ~9 nm in diameter, it was found \( H_C = 30.72 \text{ kA/m} \), at 85 K [13]. The value of coercive field depends on structural characteristics of material (domain structure, grain size, and the anisotropy of material), but also can be influenced by the interparticle interactions [26]. In monodomain particles, \( H_C \) increases with particle size increase, and vice versa in polycrystalline materials [27]. Very low increase of the \( H_C \) with annealing up to 673 K suggest that there is no significant increase in the size of lithium ferrite nanoparticles in samples S1–S3, what is in accordance with the XRD and TEM analysis (Fig. 1). In those samples the size of lithium ferrite nanocrystallites is significantly lower than the critical size, \( D_C \), below which particles possess a single magnetic domain structure (for soft ferrites, \( D_C \) is about 30–40 nm [4]). Therefore, nanoparticles of samples S1–S3 can be consider as magnetically monodomain particles. On the contrary, lower value of \( H_C \) found in sample S4 is due to the fact that the particle size, \( d \) is larger than \( D_C \).

The \( M(H) \) measurements also show that only the sample S4 is saturated in a field of 3.98 MA/m (Fig. 4), with the saturation magnetisation \( M_S = 67 \text{ Am}^{-2}/\text{kg} \). The lack of the magnetisation saturation in the high magnetic fields and at low temperatures in samples S1–S3 can be due to a non-collinear spins arrangement and/or the frustration of magnetic interactions [28]. The saturation magnetisation of samples S1–S3 have been determined by extrapolation of \( M \) vs. \( 1/H \) curves when \( 1/H \rightarrow 0 \). It can be seen that the value of \( M_S \) constantly increases with increasing annealing temperature and improving the crystalinity of lithium ferrite particles (Table 2). In bulk Li\(_{0.5}\)Fe\(_{2.5}\)O\(_4\) the saturation magnetization was found to be \( M_S(\text{bulk}) = 68.7 \text{ Am}^{-2}/\text{kg} \) at room temperature [6]. Following the theoretical Néel model which considerize two sublattices with collinear spin arrangement, and the antiferromagnetic interactions between sublattices, the magnetization per formula unit of inverse lithium ferrite at 0 K, with the cation distribution (Fe\(_{\lambda}\)\[Li_{0.5}Fe_{1.5}\]BO\(_4\)) and magnetic moments of Li\(^{+}\) (0 \( \mu_B \)) and Fe\(^{3+}\) (5 \( \mu_B \)) ions, can be calculated as: \[ |M_B| = |M_{\lambda}| = |M_{\mu}| = (0.5 \times 0 + 1.5 \times 5\mu_B) = (2.5\mu_B) \text{ Am}^{-2}/\text{kg}. \]

Generally, decrease of the saturation magnetisation, \( M_S \) of the bulk Li\(_{0.5}\)Fe\(_{2.5}\)O\(_4\) relative to the theoretically predicted value is connecting with the disalignment from the parallel spin ordering at higher temperatures. Spin disor-
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...dering is usually more pronounced in nanosized samples due to high surface-to-volume ratio and/or higher defects density. In our case, in the sample S4 the saturation magnetization at 5 K is close to the calculated value for bulk lithium ferrite at 0 K, while in the samples S1–S3 value of \( M_S \) is something lower, especially in the as prepared sample S1. In the model which suggests existence of magnetically dead surface layer, decreasing of the saturation magnetisation in an assembly of spherical NPs with diameter \( d \), relative to the bulk counterpart, \( M_S(bulk) \), can be expresses as: \( M_S(d) = M_S(bulk) (1 - 6t/d) \) [29]. It was found that the thickness of such layer would be 0.5 nm in sample S1, and 0.2 nm in samples S2 and S3. From this, we can conclude that at low temperatures the magnetic disordering exists only inside the first crystalographic layer (the lattice constant in these samples was found to be \( a = (0.833±0.001) \) nm [19]).

Taking into account that the most pronounced decrease of the saturation magnetization, i.e. the highest magnetic disordering is found in the sample S1 (what is in accordance with Mössbauer spectra analysis), we have tried to see if the effect of exchange coupling between a ferrimagnetically ordered core and a magnetically disordered shell could be observed in this sample. Therefore, the field–cooled (FC) hysteresis loop was measured at 5 K after cooling the sample in the presence of magnetic field of 3.98 MA/m, as shown in Fig. (5). A very low asymmetry of the FC hysteresis loop has been observed in the sample S1, with an exchange bias field, \( H_{EX} \approx 1.99 \) kA/m, what indicate a weak exchange coupling between a magnetically ordered core and a magnetically disorder surface shell of Li0.5Fe2.5O4 nanoparticles.

The remanence–to–saturation ratio \( R = M_R/M_S \) values obtained from the \( M(H) \) data at \( T = 5 \) K were between 0.24 and 0.29, smaller than the \( R = 0.5 \) value expected for noninteracting particles with uniaxial anisotropy [30]. The low \( R \) value (\( R < 0.3 \)) suggested that interparticle interactions are not negligible [31]. Since the dipole–dipole interactions are significant only if the net magnetic moments of individual NPs interact, we have estimated an average magnetic moment per particle. We assumed that the external magnetic field of 3.98 MA/m is strong enough to align the net magnetic moment of particles along the field, at 5 K. Than, the saturation magnetization value of selected sample S3, \( M_S(S3) = 60 \) Am\(^2\)/kg = 285.6 kA/m have been used to extract an average magnetic moment per particle. For the density, \( \rho \) of lithium ferrite powders we used the value of 4760 kg/m\(^3\) calculated from the results obtained from

![Hysteresis loops of lithium ferrite nanopowders recorded at 5 K.](image)

**Table 2. An Average Particle Size of Lithium Ferrite NPs Annealed at Different Temperatures, Estimated from XRD [17] and TEM Analysis; the Coercivity (\( H_C \)); the Saturation Magnetization (\( M_S \)); the Remanent Magnetization (\( M_R \)); and the Ratio, \( R = M_R/M_S \), were Estimated from the Hysteresis Loop Measurements at 5 K**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (XRD) (nm)</th>
<th>Particle size, ( d ) (TEM) (nm)</th>
<th>( T ) (K)</th>
<th>( H_C ) (kA/m)</th>
<th>( M_S ) (Am(^2)/kg)</th>
<th>( M_R ) (Am(^2)/kg)</th>
<th>( M_R/M_S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>~6</td>
<td>~12</td>
<td>5</td>
<td>29.76</td>
<td>49</td>
<td>14.6</td>
<td>0.29</td>
</tr>
<tr>
<td>S2</td>
<td>~6</td>
<td>~12</td>
<td>5</td>
<td>31.83</td>
<td>60</td>
<td>15.9</td>
<td>0.27</td>
</tr>
<tr>
<td>S3</td>
<td>~9</td>
<td>~12</td>
<td>5</td>
<td>31.43</td>
<td>60</td>
<td>17.7</td>
<td>0.29</td>
</tr>
<tr>
<td>S4</td>
<td>~40–90; &gt;100</td>
<td>~12</td>
<td>5</td>
<td>19.81</td>
<td>67</td>
<td>16.0</td>
<td>0.24</td>
</tr>
</tbody>
</table>
XRD analysis [19]. Considering the spherical shape of NPs with a mean particle diameter \(d = 12\) nm, \((V = \pi d^3/6,\) the volume of particle), the average single-particle magnetic moment \(\langle \mu \rangle\) was estimated to be \(\sim 27900\) \(\mu_B\), supporting our assumption that the dipole–dipole interactions between NPs are not negligible. The presence of interparticle interactions was further confirmed by the measurements of the magnetization \(M\), as a function of \(H/T\), as is shown in the inset of Fig. (5), for sample S1. The magnetization was measured at high temperatures, 275 K and 350 K. For a system of noninteracting, superparamagnetic particles, \(M\) vs. \(H/T\) curves overlap and follow a universal law: \(M = N\langle \mu \rangle(L)_x\), where \(N\) is a number of nanoparticles with magnetic moment \(\mu\), and \(L(x)\) is the Langevin function of parameter \(x = \mu H/k_B T\). Discrepancy between the \(M\) vs. \(H/T\) curves, found at high temperatures, point out on the interparticle interactions, although the presence of some bigger and blocked particles (which are not superparamagnetic at these temperatures) can not be excluded.

### 3.3. Magnetic Anisotropy Analysis

The analysis of magnetic anisotropy of the assembly of lithium ferrite nanoparticles becomes more difficult in the presence of interparticle interactions. Besides the magnetocrystalline, surface, and/or strain anisotropy, the interparticle interactions also contribute to the effective magnetic anisotropy, \(K_{\text{eff}}\) [12, 32]. In the case of strong interparticle interactions, their contribution to \(K_{\text{eff}}\) can be of the same order as the anisotropy of individual NPs, and it can strongly affect magnetic behavior of system, especially in low magnetic fields and at low temperatures [14, 33]. In order to determine the magnetic anisotropy value in the system of lithium ferrite NPs, we have used the approach suggested by J.J. Prejean and co-workers [34], where the effective anisotropy constant \(K_{\text{eff}}\) can be extracted from the hysteresis loop measurements using the relation: \(K_{\text{eff}} = 1/8 \times \text{area of the hysteresis cycle}\). Sample S3 has been taken under consideration. Following this procedure, from the area of the hysteresis loop recorded at \(5\) K, it was found: \(K_{\text{eff}}^{\text{nano}}(5\) K) = 1.04 \(\text{kJ/m}^3\). We further assumed the cubic magnetic anisotropy of bulk lithium ferrite, and used the relation between the effective and magnetocrystalline anisotropy constants \(K_{\text{eff}} = |K_1|/12 [33, 35, 36]\). Thus, we obtained a value \(|K_1^{\text{nano}}(5\) K) = 12.4 \(\text{kJ/m}^3\) for sample S3. Previously reported values for \(K_1^{\text{bulk}}\), measured in a single crystal of lithium ferrite (in ordered, \(\alpha\)-phase, S.G. \(Pm\overline{3}m\)) at 300 K [17] and 77 K [18], were found to be negative at both temperatures, i.e. \(K_1^{\text{bulk}}(300\) K) = \(-8.5\) \(\text{kJ/m}^3\) and \(K_1^{\text{bulk}}(77\) K) = \(-12.7\) \(\text{kJ/m}^3\). It has also been shown that there are no significant changes in the value of \(K_1\) at temperatures below 77 K in both, ordered (S.G. \(Pm\overline{3}m\)) and disordered (S.G. \(Fd\overline{3}m\)) spinel phases of \(\text{Li}_{0.3}\text{Fe}_2\text{O}_4\) [18]. Comparing the absolute values of \(K_1\) for bulk and nanosized lithium ferrite samples in ordered \(\alpha\)-phase (S.G. \(Pm\overline{3}m\)) at low temperatures (\(\leq 77\) K), a good agreement is obtained. The effective anisotropy constant \(K_{\text{eff}}\) can also be calculated using the relation \(K_{\text{eff}}V = 25k_BT_B\). Taking into account that the NPs are spheres with diameter (d)~12 nm, and that the \(T_B\) corresponds to the maximum of ZFC magnetization measured at field of 39.79 \(\text{kA/m}\), i.e. \(T_B \approx 265\) K, it was obtained \(|K_{\text{eff}}| = 1.01\times10^4\) \(\text{J/m}^3\). This value is two orders of magnitude higher than the value extracted from the hysteresis loop measurement. This discrepancy in the values of the effective magnetic anisotropy \(K_{\text{eff}}\) has been explained previously [14] as originated from magnetic measurements in low and high magnetic fields in a system of spherical nanoparticles with dipolar interactions. If the external magnetic field \(H\) is high enough to overcome the energy barrier, \(\Delta E \sim k_BT_B\), i.e. \(\mu H \geq k_BT_B\), (where \(\mu\) is the net magnetic moment of the particle, \(T_B\) is the blocking temperature and \(k_B\) is the Boltzmann constant), the magnetic energy \(\mu H\) will dominate the interaction energy and the contribution of the interparticle interactions to the effective magnetic anisotropy can be neglected. In the present case, the value of \(K_{\text{eff}}^{\text{nano}}\) estimated for \(\text{Li}_{0.3}\text{Fe}_2\text{O}_4\) obtained from the \(M(H)\) hysteresis loops is close to the magnetocrystalline anisotropy \(K_1\) at low temperature. Since the
hysteresis loop is recorded at very low temperature (5 K < T), and at high magnetic fields (up to 3.98 MA/m; enough high to overcome the anisotropy energy barrier which originates from interparticle interactions), the ∆E parameter will give information about single-particle anisotropy properties [32]. Similar results have been obtained in the system of Fe₃O₄ [14], and γ-Fe₂O₃ [37] nanoparticles. The contribution to K_{eff} value coming from dipolar interactions becomes more pronounced if the value of K_{eff} is estimated from measurements in low magnetic fields (of few dozens of kA/m). Then, μB < k_{B}T, and a collective behavior of an assembly of interacting NPs comes into play. It is worth to mention that, according to Yang and co-workers, increase in K_{eff} value, observed in lithium ferrite nanocrystallite, has been assigned to the contribution of internal strain [13].

It has to be noticed that the model suggested in Ref. [34], neglects the contribution from the unsaturated surface spins to K_{eff} value. Generally, the energy barrier ∆E in the core–shell model can be written as a sum of two contributions coming from the particle core (with volume V) and the shell (with surface area S), i.e., ∆E = K_{core}V_{core} + K_{surf}S [15, 28, 37]. By comparing K_{eff} value in nanosized ferrite particles with the core/shell structure with adequate value measured in bulk counterpart, we concluded that the above-mentioned method [32] is adequate to estimate the anisotropy constant value from the particle core (K_{core}).

CONCLUSIONS

We have investigated the structural and magnetic properties of lithium ferrite nanoparticles. The evidence of a core–shell structure has been found by inspection of XRD and TEM analysis, as well as Mössbauer spectroscopic and magnetic measurements. An exchange bias between the magnetically ordered core and the disordered surface has been observed in nanocrystalline samples. The magnetic behavior of the as-prepared Li₀.₅Fe₂O₃ NPs reflected the superparamagnetic behavior with dipole–dipole interactions. The thickness of the spin–disordered surface layer was estimated to be less than 1 nm. From magnetic measurements in a high-field regime, the effective magnetic anisotropy of the particle core, K_{core}, has been found to be similar to the corresponding bulk value for lithium ferrite.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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