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Abstract

Magnetic properties of iron oxide nanoparticle with spinel structure are strictly related to a complex interplay between cationic distribution and the presence of non-collinear spin structure (spin canting). With the aim to better insight into the effect of magnetic structure on magnetic properties, in this paper we investigated a family of small crystalline ferrite nanoparticles of formula $Co_xNi_{1-x}Fe_2O_4$ ($0 \leq x \leq 1$) having equal size ($\approx$ 4.5 nm) and spherical like-shape. Field dependence of Magnetization at low temperature indicated a clear increase of magnetocristalline anisotropy and saturation magnetization (higher than bulk value for $CoFe_2O_4$:~130 A m^2 Kg^{-1}) with the increase of cobalt content. Magnetic structure of nanoparticles has been investigated by Mössbauer spectroscopy under intense magnetic field (8T) at low temperature (10K). The magnetic properties has been explained in term of an evolution of magnetic structure with the increase of cobalt content. In addition a direct correlation between cationic distribution and spin canting has been proposed , explaining the presence of non collinear spin structure in term of super exchange interactions energy produced by the average cationic distribution and vacancies in the spinel structure.

1 Introduction

On entering the nanometer-scale the magnetic properties of the condensed matter show substantial differences with respect to the bulk state, leading to new physics [1] and applications [2]. Among nanostructured magnetic materials, nanoparticles are unique complex physical objects with physical properties greatly different from their parent massive materials. In fact, at the nanoscale, a multi-domain organization is energetically unfavorable and single-magnetic-domain particles are formed. The behavior of a random assembly of nanoparticles depends on both the type and strength of interparticle interactions, evolving from paramagnetic (PM)-like to ferromagnetic (FM)-like, including a spin-glass (SG)-like behavior. Due to the enhanced time and magnetization scales with respect to atomic systems, the magnetism of nanoparticles ensembles has been often called *Supermagnetism*[3,4].

Beyond the magnetic interparticle interactions, the physics of nanoparticle assemblies is influenced by finite-size effects on particle's core and by the modification of the structural and electronic properties at their surface. Among the relevant features arising from size reduction of magnetic particles, the presence of a non-collinear spin structure (spin-canting) at the particle surface deserves special attention, as it originates strong modifications in the magnetic properties. The symmetry breaking induces changes in the topology of the superficial magnetic moments and consequently in exchange integrals (through superexchange angles and/or distances between moments) leading thus to a different local surface anisotropy[5,6].

Among nanostructured materials, magnetic ferrites nanoparticles ($Me^{II}Fe_2O_4$; Me^{II} = Fe^{2+}, Ni^{2+}, Co^{2+}, etc) with spinel structure have generated much interest, not only for their technological applications, but also because the rich crystal chemistry of spinels offers excellent opportunities for the fine tuning of the magnetic properties[2,7,8]. The spinel ferrite has a face-centered cubic (*fcc*) structure in which the oxygen ions are cubic close-packed. The structure contains two interstitial sites, occupied by metal cations with tetrahedral, (T_d), and octahedral, (O_h), oxygen coordination, resulting in a different local symmetry (**Figure 1**). In general, the cationic distribution between the two sites is quantified by the inversion degree (γ), which is defined as the fraction of divalent ions in the octahedral sites. Superexchange interactions between magnetic atoms located in the same kind of interstitial sites (J_{Td-Td} and J_{Oh-Oh}) lead to two ferromagnetically ordered sub-lattices. On the other hand, the dominant antiferromagnetic interactions between magnetic ions in the T_d and O_h sites (J_{Td-Oh}) induce a non-compensated antiferromagnetic order between the two sub-lattices (ferrimagnetism). A sketch of the magnetic structure in spinel ferrites is reported in **Figure 1**. The net magnetization can be considered *a priori* proportional to the difference between the T_d and O_h sub-lattice magnetizations. Furthermore, the magnetic anisotropy is related to the cationic distribution due to the single ion anisotropy of the divalent cations, which depends on their position in the different interstitial sites[7].

In most of spinel iron oxide nanoparticles (γ-Fe_2O_3, Fe_3O_4), non-collinear magnetic structures have been ascribed to the presence of competing interactions between the two sub-lattices together with the structural surface topological disorder induced by the symmetry breaking [9–12]. This feature has also been confirmed by polarized neutron scattering[13] and Mössbauer experiments[14] in cobalt and copper ferrite, respectively. This picture allows one to consider that the magnetic properties of ferrite nanoparticles with a spinel structure are clearly related to a complex interplay between cationic distribution and spin canting, as recently it has been observed in $CoFe_2O_4$ nanoparticles, due to a disordered and non-homogeneous distribution of Fe and Co species within the nanoparticles[5,7,9,15,16].

The present paper aims to shed light on this complicated dependence. For this purpose we exploited the versatility of spinel oxide nanoparticles, which offer the unique advantage of a large tuning of their physical properties (saturation magnetization and magnetic anisotropy) by simply modifying the nature and amount of divalent cations, meanwhile leaving morphological and structural parameters almost unchanged. In particular we investigated the magnetic properties of a family of small crystalline ferrite nanoparticles of formula $Co_xNi_{1-x}Fe_2O_4$ having equal size ($\approx$ 4.5 nm) and shape, but whose composition was systematically varied between stoichiometric cobalt and nickel ferrite ($0 \le x \le 1$). These properties allowed us focusing the investigation only on the effect of the chemical composition on the magnetic structure (i.e., cationic distribution and spin canting), beyond the effect of particle volume or shape, in order to clarify the dependence of magnetic properties from the magnetic structure itself. Previous studies have reported the influence of cobalt substitution [17–19], but investigating bigger particles (i.e. negligible surface effects), and often with a large difference of average particle size among samples.

2   Experimental

2.1   Synthesis

All the investigated samples were prepared by polyol method[20–22], where polyol acts as solvent, reducing agent and surfactant. This method allows the production of a wide range of pure metals and oxides[23,24], with the possibility of tuning their chemical composition. In a typical synthesis of $CoFe_2O_4$ (Co_{100}-Ni_0 sample) 2 mmol of iron (III) nitrate nonahydrate (Sigma Aldrich, > 98 %), 1 mmol of cobalt (II) nitrate hexahydrate (Sigma Aldrich, 98 %) and 1 ml of distilled water were added to 100 ml of tri-ethylene glycol (TEG, Sigma Aldrich, 99 %) in a round bottom tree-neck flask. The solution was heated in a mantle to the boiling point and kept under reflux and mechanical agitation for 2h using a condenser; then it was cooled to room temperature. With the addition of acetone to the solution, the precipitation of a black powder was induced. The product was washed again with acetone and separated via centrifuge; this procedure was repeated three times, and finally the powder was dried in an oven at 60°C overnight. For all samples the same procedure has been employed, changing the relative amount of precursors, to obtain the desired

chemical composition (**Table 1**). The samples have been labeled Co_x-Ni_y being x and y the respective per cent amount Co and Ni cations.

2.2 Experimental techniques and data treatments

X-ray diffraction (XRD) analysis was carried out using a Seifert diffractometer with a θ-θ Bragg-Brentano geometry, with Cu-K_α wavelength. The samples, in form of powder, were analyzed on a zero-background silicon holder in the 2 θ range 10-70°. The cell parameters and the average size of the coherent crystalline domain were determined by XRD Rietveld refinement using MAUD [25,26]. To determine the instrumental broadening contribution, a polycrystalline and strain-free sample of Al_2O_3 has been used as standard.

For TEM observations, the samples powders were dispersed in isopropyl alcohol and submitted to an ultrasonic bath; then the suspensions were dropped on carbon-coated copper grids and observed using a TEM (FEI Tecnai 12 G2 Twin) equipped with an electron energy filter (GATAN Bio-filter), and a Peltier cooled charge-coupled-device-based slow scan camera (GATAN 794 IF). TEM images were analyzed with ImageJ software[27]. The contours of each particle were manually defined and, thanks to the automated measurement suite of the software, the exact particles area has been calculated. Then, assuming a spherical particle shape and knowing the area value, the diameter D has been calculated for each particle. Finally, the diameters have been fitted with a log-normal function:

$$P = \frac{A}{D\,w\,\sqrt{2\pi}} \exp - \left[\frac{\ln^2 \left(D/\langle D_{TEM} \rangle \right)}{2w^2} \right] \qquad (3)$$

where A is the area of the peak, w, the standard deviation of the natural logarithm of the variable D and $\langle D_{TEM} \rangle$ is the median of the log-normal distribution, which gives an estimation of the average particles size.

The determination of the cobalt, nickel and iron concentrations in the different samples was performed using a Perkin Elmer Dual Vision OPTIMA 2000 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Samples were digested with HNO_3 (analytic grade) on a hot plate at 80-110 °C until complete dissolution and measured after dilution with ultrapure water. The wavelengths used for Co, Fe, and Ni were 228.616, 259.940 and 231.604 nm, respectively. Chemical formulas obtained by ICP analysis are reported in **table 1**.

FT-IR spectra were collected in the region from 400 to 4000 $cm-1$, using a Bruker Equinox 55 spectrophotometer. Nanoparticles were analyzed dispersing the powders in KBr pellets or, for pure TEG, dropping the liquid over pure KBr pellets.

TGA-SDTA measurements were performed using a Mettler-Toledo TGA/SDTA 851. The data were collected in the range 25-1000 °C with a heating rate of 10 °C min^{-1} under oxygen flow (flow rate of 50 ml/min).

^{57}Fe Mössbauer spectra were recorded using a ^{57}Co/Rh γ-ray source mounted on an electromagnetic transducer with a triangular velocity form. The samples consist of a thin layer of about 40 mg of the powdered compound located in a sample holder. The spectra were obtained at 10 K in an 8 T field oriented parallel to the γ–beam, and were then analyzed by using the program 'Mosfit'[28–31]. The hyperfine structure was modeled by means of a least-square fitting procedure involving Zeeman sextets composed of Lorentzian lines. To describe the broadening of lines, several magnetic subcomponents have been considered where isomer shift, quadrupolar shift, linewidth and effective field values were free during the refinement as well as the intensities of intermediate lines (2,5) result of the angle between the hyperfine field and the γ-beam; while the ratio of absorption areas of external/internal lines is systematically equal to 3. The isomer shift (IS) values were referred to that of α-Fe at 300 K.

DC magnetization measurements were performed by a Quantum Design SQUID magnetometer, equipped with a superconducting coil (H$_{max}$= ± 5 T). To avoid any movement of the nanoparticles during the measurements, the samples, in form of powders, were immobilized in epoxy resin. The saturation magnetization M_S was extrapolated fitting the curves at high field using the Law of Approach to Saturation (LAS)[32]:

$$M = M_S \left(1 - \frac{A}{H} - \frac{B}{H^2}\right) \quad (4)$$

where A and B are constant parameters.

The irreversible switching behavior was analyzed studying the field dependence of remanent magnetization by direct current demagnetization (DCD) protocol[33,34]. In this protocol, the sample was saturated in a field of -5 T, than the field was removed and the remanence magnetization measured. A small field was applied to reverse the magnetization (H$_{rev}$ = 0.01 T); then it was removed, and again the remanence was measured. This process was repeated increasing the H_{rev} step by step up to 5 T.

3   Results and discussion

The X-ray diffraction (XRD) patterns (**figure 2**) exhibit the common Bragg peaks typical of a cubic spinel structure (PDF card 22-1086) for all the samples. No other phases are detected. The size of the coherent crystalline domain and the value of the lattice parameters **a (table 1)** have been evaluated for each sample by means of Rietveld refinement (**figure S1**); **a** becomes smaller increasing the Ni amount [35], as expected due to the larger ionic radius of Co^{2+} (≈ 0.58 Å in T$_d$ and ≈ 0.75 Å in O$_h$ coordination) with respect to that of

Ni^{2+} (≈ 0.55 Å in T_d and ≈ 0.69 Å and O_h coordination) [36,37]. It is worth of mention that the parameters **a** are larger than expected considering the bulk values of ≈ 8.38 Å and ≈ 8.33 Å for pure cobalt and nickel ferrite, respectively [37–39] especially for sample Co_0-Ni_{100} (pure nickel ferrite). TEM images (**figure 3**) show high crystalline spherical-like particles with a high degree of aggregation, which is particular evident in sample Co_0-Ni_{100} (**figure 3e**). Electron diffraction confirms the presence of a unique spinel phase (a representative example is shown in **figure 3f** for sample Co_{100}-Ni_0). Particle size distributions (symbols in **figure 3g**) are well fitted by using log-normal functions (lines in **figure 3g**) for all the samples, showing a relative low polydispersity. The mean particles size extracted by TEM are equal for all the samples ($<D_{TEM}> \cong 4.6$ nm) and always lower that mean crystallite size estimated from XRD analysis ($<D_{RV}> \cong 5.7$ nm). We should however remind that the presence of the residual coating produces a high background, especially for sample Co_0-Ni_{100} at low angle. Such background can interfere with the estimation of the peaks broadening, inducing an important error in the estimation of particles size. In order to clarify this point, an estimation of the magnetic diameter has been obtained by the activation volume (details in **Supporting Information**). Sample Co_{50}-Ni_{50}, has been considered as a model: its magnetic viscosity S was measured in the range of H_{rev} between 0.2 T and 1.2 T, being the coercivity 0.50 T (**figure S2**). Assuming a system composed of spherical particles, the obtained V_{act} corresponds to a mean magnetic grain diameter of 4.7(5) nm, in perfect agreement with TEM measurement of 4.6(1) nm. This result suggests that the larger XRD diameter can be due to the polyol coating explaining the unexpected low value of sample Co_0-Ni_{100}, where the residual TEG represent 35% of the weight from TGA evaluation.

3.1 Magnetic Properties

Since all the samples are made up of crystalline spherical-like particles that, within the experimental error, have the same average size, any difference in magnetic properties can be ascribed to the effect of the chemical composition.

At 5 K, all samples behave as blocked ferrimagnets (**figure 4**); a significant decrease of the magnetic anisotropy is observed with the decrease of cobalt content, as it is shown by the monotonic decrease of the coercive field *(μ_0H_C ,* **table 2**)). This behavior is confirmed by the irreversibility field (which was evaluated as the point in which the difference between the magnetizing and demagnetizing branches is under the 1% of their maximum value)[33] that can be defined as the saturation field (μ_0H_{sat} , **table 2**), i.e., the maximum field which is necessary to apply to reverse all the superspins. Co^{2+} ions produce a marked magneto-crystalline anisotropy far above that of Ni^{2+} and Fe^{3+} ions; indeed its orbital magnetic moment is not quenched by the crystal field, and a spin-orbit coupling occurs, particularly strong for Co^{2+} ions located in octahedral sites[40–42]. Bulk $CoFe_2O_4$ crystals, have a strong cubic magnetic anisotropy, but such behavior is usually suppressed with particles size under 5 nm, and an uniaxial anisotropy is observed [43,44]. The reduced remanence magnetization (M_R/M_S) should be ≈ 0.8 and 0.5 for cubic and uniaxial anisotropy, respectively [3,44–46].

Analyzing the M_R/M_S value of sample Co_{100}-Ni_0, only a small tendency towards cubic anisotropy is observed, furthermore, reducing the cobalt content, a reduction of M_R/M_S values is observed. *The very low value of $\approx$ 0.29 measured for Co_0-Ni_{100} could be ascribed to the effect of strong dipolar interactions on a relative soft material[47], to the presence of frustrated surface spins[45] or to thermal demagnetizing effects . To verify the role of surface effect, an hysteresis loop at 5K was recorded after cooling the sample in an applied field of 3T (see figure S3a in supporting information). Any shift of the hysteresis loops is observed in FC conditions, allowing to rule out the presence of high anisotropic surface shell. Also a preliminary investigation of interparticle interactions has been carried out by means of ΔM plots (Figure S3b and Supporting Information for details on the experimental method): only relative small dipolar interparticle interactions are observed. Then , due to the distribution of values of magnetic anisotropy energy, it is more likely that a fraction of particles is in the superparamagnetic state even at 5 K (temperature used for the measurement), thus reducing the M_R/M_S values.*

In the simplest approximation of Stoner and Wohlfarth[48] (i.e., single particle with uniaxial anisotropy), the relation between the anisotropy constant *K* and the anisotropy field $\mu_0 H_K$ can be defined as [3,49]:

$$K = \frac{\mu_0 H_K M_S}{2} \qquad (5)$$

*From equation 5 a roughly approximated value of the effective anisotropy constant can be obtained assuming negligible the deviation toward cubic anisotropy and the influence of interparticles interactions[33,50], and considering $\mu_0 H_{sat} \approx \mu_0 H_K$. The latter assumption has been first suggest by Kodama et al for $NiFe_2O_4$ nanoparticles[51] and it has been used for other similar nanoparticles systems[44,52,53]. The estimated values of K_{eff} show again a downward tendency with decreasing of Co content (**table 2**), confirming the decrease of magnetic anisotropy. Despite the obtained values can be considered only as a first rough approximation of K_{eff} it is worth to underline that all of them are higher than those reported for bulk and nanostructured cobalt ($\sim 1 - 4 \cdot 10^5 \, J \, m^{-3}$)[33,50,54] and nickel ferrites ($\sim 1 \cdot 10^4 \, J \, m^{-3}$)[55,56].*

It is interesting to note that the susceptibility measured at high field (i.e., the derivative of M vs H curves at 5 T), which can be considered directly related to the surface component of anisotropy[51], follows the same trend of the effective anisotropy, suggesting that even the local surface anisotropy is enhanced by the strong single ion anisotropy of cobalt.

The field dependence of the remanent magnetization measured using the DCD protocol describes the irreversible reversal process of the magnetization. The differentiated remanence curve, consisting of the derivative of M_{DCD} with respect to H_{rev} ($\chi_{irr} = dM_{DCD}/d\mu_0 H$), represents the irreversible component of the susceptibility. This quantity can be correlated to the distribution of particles coercive fields (**figure 4c**), and it is generally called the switching field distribution (SFD) [53], providing thus a qualitative estimation of the

energy barrier distribution. Confirming the picture described by M *versus* H curves, the anisotropy energy is reduced by reducing Co amount, with a monotonic tendency.

Assuming the atomic magnetic moment of 5 μ_B for Fe^{3+}, 3 μ_B for Co^{2+} and 2 μ_B for Ni^{2+} resulting from their electronic configuration [6,18], and considering the antiparallel arrangement of moments between tetrahedral and octahedral sites for the inverse spinel structure, the magnetization is expected to decrease when reducing the Co content at the advantage of Ni one. As listed in **table 2**, the experimental values of saturation magnetization confirm this hypothesis. It is worth to mention that Co_{100}-Ni_0 possesses a relative high value of magnetic saturation, compared to that of the bulk values (83 - 90 A m^2 kg^{-1})[57], and also to those reported for highly crystalline cobalt ferrite nanoparticles[58]. In order to confirm this unexpected result the M vs H measurements in the high field region has been performed on several samples prepared in the same conditions and gave reproducible results 130 ($\pm$20 A m^2Kg^{-1}) . On the other hand, a relatively low value is estimated in the case of Co_0-Ni_{100} (for bulk it is around 55 A m^2 kg^{-1}[59]). In this framework, the interplay between inversion degree and magnetic disorder (i.e., magnetic structure) should play a key role[6,15].

3.2 Magnetic Structure

In order to understand the evolution of the magnetic properties with the chemical composition of the materials, a careful investigation of magnetic structure has been performed by [57]Fe Mössbauer spectrometry the presence of intense magnetic field at 10K. In contrary to zero-field measurements, which provide mean values of hyperfine parameters, in-field studies allow a reliable distinction between T_d and O_h Fe site components in the case of ferrimagnets: the applied field is usually added to the T_d-site hyperfine field and subtracted from the O_h-site one, because in these Fe-based oxides the hyperfine field is opposite to the magnetic moment, being negative the dominant Fermi contact term. Furthermore, in the presence of an external magnetic field parallel to the γ-ray direction, the relative areas of the intermediate lines (2,5) give relevant information about the degree of alignment of the atomic Fe magnetic moment with the applied field.

Figure 5 compares [57]Fe Mössbauer spectra recorded at 10 K under a magnetic field of 8 T applied parallel to the γ-beam on the Co_{100}-Ni_0, Co_{50}-Ni_{50} and Co_0-Ni_{100} samples. The spectra are consistent with a well blocked ferrimagnetic structure without any superparamagnetic relaxation states. The hyperfine parameters do not evidence at all the presence of Fe^{2+} ions, and the isomer shift values allow us to attribute clearly the two sextets to the Fe^{3+} in tetrahedral and octahedral sites (**table 3**), and to estimate their respective proportions from the relative absorptions areas.

From the modelling of the in-field Mössbauer spectrum both the effective field B_{eff} and the canting angle ϑ (angle defined by the direction of the effective field and the γ-beam direction) have been estimated for both tetrahedral and octahedral iron components, allowing thus their respective hyperfine field B_{hyp} to be calculated (**table 3**). When the second and fifth lines have a non-zero intensity, they evidence a non

collinear magnetic structure for Fe^{3+} magnetic moments with respect to the applied field (canted structure) [12,60]. The angle ϑ is calculated from the area ratio of second and fifth lines ($I_{2,5}$) on those of first and sixth lines ($I_{1,6}$) (**see supporting information for details**). It is worth of mention that an asymmetrical broadening of the lines in site O_h for sample Co_0-Ni_{100} was observed, probably due to the chemical disordered occupation of these sites, producing a wide range of possible chemical environments of Fe ions.

According to the absorption area ratio of the two sextets, the accurate value of the Fe^{3+} distribution between T_d and O_h sites has been estimated assuming the same values of the recoilless f Lamb-Mössbauer factor for these two species (**table 3**)[61]. ICP analysis has confirmed the 2:1 ratio between Fe^{3+} and divalent cations (i.e., Co^{2+} and Ni^{2+}), thus, considering the hypothesis of absence of vacancies, the inversion degree γ, representative of the cationic distribution, can be defined as the amount of divalent ions in octahedral sites[62]. γ was estimated at 0.74(1) and 0.78(1) for Co_{100}-Ni_0 and Co_{50}-Ni_{50}, respectively, in agreement with values usually reported for cobalt ferrite ($\gamma \approx 0.7 - 0.8$)[58,63,64]. For sample Co_0-Ni_{100} γ was estimated at 0.44(1), significantly different from that expected for pure nickel ferrite ($\gamma \approx 0.9 - 1$)[22,64]. From these results, the cationic distribution was estimated. For Fe^{3+}, $Co^{2+}$and Ni^{2+} have been considered the magnetic moment values of 5 μ_B, 3 μ_B and 2 μ_B, respectively. For simplicity, for sample Co_{50}-Ni_{50} has been defined an equivalent divalent cation Me^{2+} formed by a population of 40 % of Co and 60 % Ni, according to ICP data, with an average moment of 2.4 μ_B. Finally, considering the effect of the canting angles, the corresponding theoretical magnetization saturation values have been calculated as 90(1), 78(1) and 89(1) A m^2 Kg^{-1}, for Co_{100}-Ni_0, Co_{50}-Ni_{50} and Co_0-Ni_{100}, respectively. Only for Co_{50}-Ni_{50} this value is comparable with the experimental one, inducing to hypothesize a non-homogeneous cationic distribution for Co_{100}-Ni_0 and Co_0-Ni_{100} samples. A more representative effective inversion degree γ_{sat} has been calculated considering the effective magnetic moment per unit formula (μ_F^{exp}) calculated on the experimental saturation magnetization. This depends on the magnetic moment of each site by the relation (6):

$$\mu_F^{exp} = \left[\mu_{Fe-Oh}^{exp} + x \cdot \mu_{Me^{2+}}\right] - \left[\mu_{Fe-Td}^{exp} + (1-x)\,\mu_{Me^{2+}}\right] \qquad (6)$$

where μ_{Fe-Oh}^{exp} and μ_{Fe-Td}^{exp} represent the experimental magnetic moment of iron in O_h and T_d sites respectively, and $\mu_{Me^{2+}}$ represents the magnetic moment of the divalent cation, with x its population in O_h sites. x corresponds to the effective inversion degree γ_{sat} and can be evaluated rewriting equation (6):

$$\gamma_{sat} = \frac{\mu_F^{exp} - \mu_{Fe-Oh}^{exp} + \mu_{Fe-Td}^{exp} + \mu_{Me^{2+}}}{2\mu_{Me^{2+}}} \qquad (7)$$

Fixing the iron distribution in T_d and O_h sites according to Mössbauer results (Fe_{Td} and Fe_{Oh} , respectively), with the correction for their respective canting angles ϑ_{Td} and ϑ_{Oh} the effective magnetic moment per of

iron in T_d and O_h site can be evaluated as $\mu^{exp}_{Fe-Oh} = 5\mu_B \, cos(\vartheta_{Td}) \, Fe_{Td}$ and $\mu^{exp}_{Fe-Td} = 5\mu_B \, cos(\vartheta_{Oh}) \, Fe_{Oh}$. Thus, considering an experimental error of ± 10° for the canting angle [16,65], the values of inversion degree have been calculated as γ_{sat} = 1.00(2), 0.78(2) and 0.00(2), for MF1, MF3 and MF5, respectively. The value for Co_{50}-Ni_{50}, in agreement to that estimated from in-field Mössbauer spectra, leads to the effective formula $(Co_{0.12}Ni_{0.10}Fe_{0.78})[\ Co_{0.28}Ni_{0.50}Fe_{1.22}]O_4$, where parentheses indicate the tetrahedral coordinated cations, and brackets the octahedral ones. The value of γ_{sat} = 1.00(2) for sample Co_{100}-Ni_0 is translated in the formula $(Fe_{0.74}\square_{0.26})[Co_{1.00}Fe_{1.26}]O_4$, with vacancies in T_d sites and a overpopulation of O_h sites . This magnetic structure justifies the elevated value of MS ≈ 130 A m^2 Kg^{-1} observed in this sample. The 13 % overpopulation of octahedral sites introduces only small distortions which are not detectable in XRD pattern, but that can explain the slight increment in the lattice parameter with respect to the bulk value[66]. The result for sample Co_0-Ni_{100} leads to cationic distribution $(Ni_{1.00}Fe_{0.44})[\ Fe_{1.56}\square_{0.44}]O_4$, explaining at the same time the low saturation and the unusual iron distribution from Mössbauer spectrometry. This overpopulation of tetrahedral sites (≈ 44 %) finds a correlation in the high magnetic anisotropy constant with respect to the bulk [67,68] and in the quite large lattice parameter (≈ 8.36 Å *versus* 8.33 Å of bulk), although this parameter remains strongly dependent on the synthesis conditions.

These cationic distributions allow to estimate the environment surrounding the Fe^{3+} ions and to explain the measured canting angles. In a spinel ferrite structure each tetrahedral (Fe^{3+}) is surrounded by 12 nearest-neighbors octahedral ions, while an octahedral [Fe^{3+}] ion owns only six tetrahedral nearest-neighbors[61]. As illustrated in **figure 6**, we can assume a statistical average environment for each site of samples Co_{100}-Ni_0, Co_{50}-Ni_{50} and Co_0-Ni_{100}, involving also the presence of some vacancies. According to the molecular field theory, the superexchange interaction energy (SE) J_{TdTd} and J_{OhOh} are negligible compared to the J_{TdOh}[69]. Thus, in first approximation, considering the energy of (Fe^{3+})– O^{2-}–[Co^{2+}] comparable to that of (Fe^{3+})– O^{2-}– [Ni^{2+}] and equal to $J_{TdOh}{}^1$ = 13.7 K, and for (Fe^{3+})– O^{2-}–[Fe^{3+}] as $J_{TdOh}{}^2$ = 20.1 K[9,61], we can qualitatively estimate the SE energy for Fe^{3+}. For sample Co_{100}-Ni_0 the SE energy allows an average canting of ≈ 10° for (Fe^{3+}). The lower SE energy for [Fe^{3+}] is the origin of its higher value of canting angle (≈ 18°). Co_{50}-Ni_{50} sample owns a smaller difference between the SE energy of the two sites, which is responsible for the close and relatively high values of ≈ 18° and ≈ 22° for (Fe^{3+}) and [Fe^{3+}], respectively, where the last one owns the lower SE energy and the higher canting angle. Finally, in sample Co_0-Ni_{100} the large presence of vacancies around (Fe^{3+}) does produce a low SE energy giving rise to a canting of ≈ 18° ; furthermore the low amount of iron in tetrahedral sites produces an even lower SE energy for [Fe^{3+}], resulting in a strong canting angle of ≈ 38°[55,56]. This increase of magnetic disorder observed going from Co_{100}-Ni_0 to Co_0-Ni_{100} samples can be then ascribed to cationic distribution, influencing chemical surrounding of the iron atoms.

4   Conclusions

The properties of spinel ferrites are directly related to their chemical composition. In this work it is shown how it is possible to finely tune the magnetic behavior in Ni-Co ferrite nanoparticles by controlling the chemical composition, beyond the effect of the particle size. The evolution of the magnetic behavior with respect to the different chemical composition has been provided both by M *versus* H and DCD and their derivative curves. It is clear that increasing the cobalt content, a stronger magnetocrystalline anisotropy was produced, and higher saturation magnetization is obtained. To study the magnetic structure of the samples, and in particular to understand the unusual saturation magnetization of samples Co_{100}-Ni_0, Co_{50}-Ni_{50} and Co_0-Ni_{100}, ^{57}Fe Mössbauer spectrometry under intense magnetic field was employed. The cationic distribution between the two Fe sublattices has been estimated, and, matching this information with the saturation magnetization, it was possible to propose a cationic distribution in both T_d and O_h sites, with the presence of vacancies and an unusual overpopulation of specific sites. In addition, a spin canted structure was evidenced and explained in terms of superexchange interactions energy produced by the average cationic distribution and vacancies in the spinel structure. This study represents an example of further development in the understanding of the link between the structure and magnetic behavior of ferrite nanoparticles beyond the volume effect. This is of fundamental importance for the development of the engineering of magnetic ferrite nanomaterials for technological applications.

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