In-field Mössbauer characterization of MFe$_2$O$_4$ (M = Fe, Co, Ni) nanoparticles

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Abstract. Nanoparticle samples of Fe$_3$O$_4$, CoFe$_2$O$_4$ and NiFe$_2$O$_4$ with mean sizes in the 5-8 nm range and excellent crystallinity have been synthesized by thermal decomposition of organic precursors. Mössbauer spectra taken at 4.2 K in applied fields from 0 to 12 T could be fitted with two sextets corresponding to the A and B Fe sites of the spinel structure. The cation distribution was deduced from the relative intensities of both sextets. The Fe oxide spectrum was more similar to γ-Fe$_2$O$_3$ than to Fe$_3$O$_4$, suggesting this sample has undergone partial or total oxidation. A small residual intensity at lines 2 and 5 reveals some spin canting at both Fe sites, however the absence of a third sextet indicates that a “core-shell” spin structure, with disordered spins near the surface, does not occur in these nanoparticles.

1. Introduction
Ferrites of formula MFe$_2$O$_4$ are an important class of iron oxide materials which have long been of scientific and technological interest. In more recent years the interest in nanosized ferrites has grown tremendously, fundamentally in reason of their potential use for biomedical applications [1,2]. Several methods have been used to produce nanocrystalline ferrites, such as mechanical milling, coprecipitation, synthesis in reverse micelles, sol-gel, and others. Recently, a new synthesis method by thermal decomposition of an organic precursor has been described [3,4], which provides samples with homogeneous morphology, a good control over grain size, and improved crystallinity of the particles. Using this method we have prepared various samples of nanoparticles (NPs) of the title compounds. One sample of each composition was chosen for a complete magnetic characterization, in order to investigate the influence of the M$^{2+}$ ion on the magnetic properties. Experimental determination of the anisotropy constant $K_{\text{eff}}$ has been reported elsewhere [5].

In this work we have investigated the same samples by Mössbauer spectroscopy in applied magnetic fields at low temperature. The reasons for carrying out this kind of experiment are, at least, twofold. (1) To fully understand the magnetic properties it is important to know how the magnetic ions (specifically iron) are distributed among the two possible sites, namely the A (tetrahedral) and B (octahedral) sites of the spinel structure. Mössbauer spectra are best suited for this purpose, however the hyperfine fields at both sites are often very similar and the corresponding sextets are poorly resolved. Application of a field remedies this shortcoming since the sextets become well separated due to the ferrimagnetic spin ordering. (2) Using in-field Mössbauer spectra it has been discovered [6] that Fe oxide NPs are constituted by an inner core of ferrimagnetically ordered spins surrounded by a layer of misaligned spins; such a configuration, which later came to be known as the “core-shell model” [7],
can be best observed with this technique. A quantitative study on the thickness of the disordered layer as a function of applied field in NiFe₂O₄ NPs has recently been published [8].

2. Materials and methods

The investigated compounds were prepared by high-temperature solution reaction. For obtaining magnetite (Fe₃O₄) NPs, Fe(III) acetylacetonate, 1,2-octanediol, oleylamine, oleic acid and diphenyl ether were mixed and vigorously stirred under a nitrogen flow. The mixture was heated to 265 °C and kept in reflux condition for two hours. Ethanol was added to the solution and the oxide powder was precipitated by centrifugation. Similarly, CoFe₂O₄ and NiFe₂O₄ NPs were prepared by adding Co(acac)₂ or Ni(acac)₂ in the required proportion. Elemental analysis was carried out by the ICP-AES method, yielding empirical formulas Fe₃.₀O₄, Co₀.₉Fe₂.₁O₄ and Ni₀.₈Fe₂.₂O₄. Structural characterization was done by x-ray diffraction (XRD) and transmission electron microscopy (TEM). Mössbauer spectra were collected at T = 4.2 K under fields \( H = 0, 4, 8 \) and 12 T provided by a Cryogenic™ superconducting magnet and parallel to the γ-ray direction. A ~30 mCi \(^{57}\)Co source was driven sinusoidally in a field-free region of the cryostat.

3. Results and discussion

XRD diagrams of all samples indicated a single phase with the spinel structure. TEM images showed nearly spherical and well-crystallized nanoparticles. The NP diameter distribution was fitted to a log-normal function, yielding the following mean diameters \( \langle d \rangle \) and (in parentheses) standard deviations \( \sigma \): Fe₃O₄ 6.2 nm (0.13), CoFe₂O₄ 5.3 nm (0.18), and NiFe₂O₄ 8.1 nm (0.17). Mean diameters deduced from XRD diagrams by use of Scherrer’s formula are very similar to the latter ones, indicating that no particle agglomeration has occurred; indeed, the product of this synthesis are NPs coated with oleic acid, which acts as a surfactant.

Mössbauer spectra at room temperature are superparamagnetic doublets, as expected. The 4.2 K spectra in various fields are shown in figures 1, 2 and 3. All spectra could be satisfactorily fitted with two magnetic sextets; the line intensities were taken in the ratio 3:q:1 where q was left free to vary for each sextet. Anticipating the possibility of a core-shell structure [8], we also tried a model with three sextets, but the fit usually converged to nonphysical values of some parameters such as linewidth, intensity, etc. and in any case did not improve the fit quality. The area ratio between the two sextets,
obtained at the higher fields, was used as a constraint in fitting the lower-field, less-resolved spectra. Due to the ferrimagnetic spin ordering, the effective field that increases (decreases) for increasing applied field can be unambiguously associated to Fe ions placed at the A (B) site. The linear dependence $B_{eff} = B_{hf} \pm B_{app}$ is illustrated in figure 4.

Figure 3. Mössbauer spectra of Fe$_3$O$_4$ sample at indicated fields. Fitted subspectra are shown by continuous lines.

Figure 4. Effective fields vs. applied field for Fe$_3$O$_4$ sample, showing that $B_{app}$ adds to or subtracts from the hyperfine field $B_{hf}$ at each site.

Table 1 shows the most relevant hyperfine parameters obtained by fitting, i.e. the hyperfine fields $B_{hf}(A)$ and $B_{hf}(B)$, the isomer shift difference $\Delta IS = IS(B) - IS(A)$ and the B/A sextet area ratio. It is not meaningful to quote IS values separately owing to uncertain temperature corrections. Quadrupole shift values were always smaller than 0.1 mm/s.

|       | $B_{hf}(A)$ | $B_{hf}(B)$ | $\Delta IS$ | $I_B/I_A$ |
|-------|-------------|-------------|-------------|-----------|
| CoFe$_2$O$_4$ | 50.1(1)     | 53.3(1)     | 0.13(2)     | 1.68      |
| NiFe$_2$O$_4$ | 49.6(1)     | 52.8(1)     | 0.14(5)     | 1.25      |
| Fe$_3$O$_4$   | 49.8(1)     | 52.4(1)     | 0.10(3)     | 1.56      |

In addition to the data listed above, a very important quantity is the second-to-third line intensity ratio $q$, from which the mean canting angle can be estimated according to the expression

$$q = \frac{4 \langle \sin^2 \theta \rangle}{2 - \langle \sin^2 \theta \rangle}$$

The investigated compounds will be discussed separately in the following.
3.1. Co ferrite
For $M = \text{Co}$, our data yielded a $B/A$ ratio equal to 1.68. Combining this result with the chemically determined stoichiometry, one obtains the structural formula $(\text{Co}_{0.20}\text{Fe}_{0.80})_A[\text{Fe}_{1.34}\text{Co}_{0.66}]_B\text{O}_4$, showing that some cation exchange has taken place ($\text{CoFe}_2\text{O}_4$ is an inverse spinel in bulk form). Regarding parameter $q$ (equation 1), both sites showed spin canting, the one at $A$ decreasing for increasing field and the one at $B$ remaining constant around 20°.

3.2. Ni ferrite
For $M = \text{Ni}$, $B/A = 1.25$ yielding $(\text{Ni}_{0.02}\text{Fe}_{0.98})_A[\text{Fe}_{1.22}\text{Ni}_{0.78}]_B\text{O}_4$; this sample is thus an almost perfectly inverse spinel. The canting angle at both Fe sites was $(20\pm5)^\circ$ and insensitive to the applied field.

3.3. Fe oxide
Data for the Fe oxide give $B/A = 1.56$, which differs significantly from the 2:1 ratio expected for $\text{Fe}_3\text{O}_4$. It thus appears that our sample, nominally magnetite, has oxidized to maghemite after preparation. This conclusion is supported by the fact that the measured spectra are a sum of only two sextets; otherwise, the zero-field spectrum at low temperature should be more complex, with various shoulders as shown by $\text{Fe}_3\text{O}_4$ below the Verwey transition temperature [9]. Spin canting angles were similar to those observed in Ni ferrite.

3.4. Spin structure of the nanoparticles
The spectra fitting with only two sextets implies the absence of a significant fraction of randomly canted Fe spins on the particle’s surface, since otherwise a third sextet, with broad lines, would be required to fit the in-field spectra [6,8]. The absence of such a “core-shell” spin arrangement in samples produced by the high-temperature reaction method has been observed in other recent studies [10,11] and has been attributed to the organic coating, which might reduce the particle’s surface anisotropy. On the other hand, we have no explanation for the observed spin canting at both sites in the ferrimagnetic core, although canting at the $B$ site is not unusual in ferrites [12].

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