A Mössbauer effect study, as the main key to the investigation of anomalous magnetic properties of MnZn nanoferrite

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Abstract
In this research, a low temperature in-field 57Fe Mössbauer spectroscopy is used for investigation of anomalous magnetic properties of MnZn nanoferrite. Based on Mössbauer spectroscopy results, the reduced saturation magnetization of MnZn nanoferrite in respect to that of bulk sample is due to nonequilibrium cation distribution and spin disorder. The enhanced Curie temperature of MnZn nanoferrite in respect to that of bulk sample can be attributed to the strengthening of the (A)-O-[B] superexchange interactions due to an increase of the magnetic ion concentration in the (A) site.

Keywords: ferrimagnetic materials, Mössbauer effect, hyperfine interactions

1. Introduction
57Fe Mössbauer spectroscopy is a nuclear-probe technique that is very well suited for the investigation of the local symmetry, the magnetic state, and the charge states of iron ions in iron-containing materials. This sensitivity is due to interactions of the 57Fe nuclei with their surroundings. In spinel ferrites, MFe2O4 (M is a divalent metal cation), Mössbauer spectra are often dominated by magnetic interactions. The splitting of the characteristic six line spectra reveals the local magnetic fields at the positions of the Mössbauer nuclei. At room and at lower temperatures, these fields often are of the order of 50 T [1]. The origin of such high local fields in spinel ferrites is due to an indirect-exchange interaction (superexchange) between nuclear spins, where the spin density is transferred via the oxygen anions [2]. As a consequence of this supertransfer mechanism, a particular iron ion experiences local fields that reflect the distribution of magnetic (ferric) ions in its neighborhood. This is particularly true for ions in octahedral coordination [2].

The ability to readily provide information about the noncollinearity of spins in magnetic structures is one of the great advantages of Mössbauer spectroscopy. The relative intensities of second (I2) and fifth (I5) lines in magnetically split six-line spectra depend on the angle between the magnetic hyperfine field and the gamma ray direction [2]. Thus, by applying an external magnetic field with sufficient strength, one can study the degree of alignment of the spins along the field direction. When the aligned moments are composed of canted local spin moments, the directions of the magnetic hyperfine fields are no longer parallel to the external field and both I2 and I5 will change. The canting angle θ can be calculated from the line intensities of the magnetically split Mössbauer spectra.

The magnetic moments of the nanoscale mechanically treated ferrite particles undergo, above a certain temperature, spontaneous thermal fluctuations, analogous to the behavior of paramagnetic atoms, and exhibit a so-called superparamagnetic behavior [3]. Because of its great sensitivity to these magnetic fluctuations, Mössbauer spectroscopy was found to be a suitable technique for their detection. Such magnetic fluctuations can, however, complicate the analysis of spectra by a collapse of the magnetic hyperfine field far below the Néel temperature and give rise to relaxation line broadening or—even down to very low temperatures—to unresolved hyperfine-field distributions.

Quadrupolar interactions of the Mössbauer nuclei reflect local symmetry. Here, the symmetry of the charge distribution experienced through the electric field gradients sets up the charges surrounding the nuclei. In the case of ferric ions, this interaction is dominated by
the distribution of ionic charges in the lattice. On the other hand, the isomer shift interaction reflects the electron density at the nuclei. This interaction causes a marked dependence of the position of the Mössbauer transition on the charge state of the Mössbauer ion [4] and, to a lesser extent, on the geometry of its coordination.

The spinel structure consists of an almost perfect fcc arrangement of anions, wherein cations are located in sites of tetrahedral and octahedral coordination forming an ordered array in the interstices provided by the anions. Thus, the structural formula of a spinel ferrite in detail reads \( \text{M}^{2+}[^{\text{B}}]_{\text{x}} \text{Fe}^{3+}[^{\text{B}}]_{\text{y}} \text{O}_4 \), where the round and square brackets enclose species in sites of tetrahedral (A) and octahedral (B) coordination, respectively; \( \lambda \) represents the so-called degree of inversion [defined as the fraction of the (A) sites occupied by \( \text{Fe}^{3+} \) cations]. In the structure, each tetrahedrally coordinated cation is surrounded by twelve [B]-site ions (each oxygen ion is surrounded by three [B]-site ions). On the other hand, each cation at a [B] site has six (A)-site nearest neighbors [5].

A characteristic property of the supertransfer mechanism in spinel ferrites is given by its strong dependence on the extent to which the spin density is transferred from one interacting cation to another via an intermediate ion. This causes a dependence of local magnetic fields on the cation–anion distance and on the angle formed by the two interacting cations and the intervening oxygen ion. The supertransfer mechanism is most effective if the two cations involved are located on opposite sides of an anion, forming an angle of 180°. Although this configuration does not occur in spinel ferrites, it has been found that the (A)-O-[B] angle of about 126° still results in a significant interaction. On the other hand, the 90° [B]-O-[B] and, in particular, the (A)-O-(A) interaction is magnetically less favorable either because of the smaller angles involved or because of the larger cation–anion distances [6]. The more covalent \( \gamma \)-ray direction. The velocity scale was calculated from the subspectral intensities (I(A)/I(B) = \( \lambda \)) [13]. The average canting angle, \( \psi \), was calculated from the ratio of the intensities of lines 2 and 1, I(2)/I(1), according to \( \psi = 90° - \arcsin(\lambda/2) \).

3. Results and discussions

The low-temperature (4.2 K) Mössbauer spectra of mechanochemical ferrites, MnFe₂O₄, and ZnFe₂O₄, and Mössbauer studies [10], magnetic properties and morphology of nanocrystalline Mn₀.₅Zn₀.₅Fe₂O₄ [11]. It is interesting to mention that the magnetization of mechanosynthesized Mn₀.₅Zn₀.₅Fe₂O₄ estimated the value of the saturation magnetization of mechanosynthesized Mn₀.₅Zn₀.₅Fe₂O₄ to be approximately 82.7 emu/g, which is about 41% lower than the value reported for bulk Mn₀.₅Zn₀.₅Fe₂O₄ (140 emu/g) [11].

The second important observation is that the mechanosynthesized Mn₀.₅Zn₀.₅Fe₂O₄ exhibits an enhanced Néel temperature. The Néel temperature of Mn₀.₅Zn₀.₅Fe₂O₄ estimated the measured temperature of mechanosynthesized Mn₀.₅Zn₀.₅Fe₂O₄, compared with the bulk Mn₀.₅Zn₀.₅Fe₂O₄.

To elucidate this anomalous behaviour, we performed low-temperature in-field \( ^{57} \text{Fe} \) Mössbauer measurements. These experiments enable us to determine both ionic configuration and spin arrangement in the mechanosynthesized MnZn ferrite nanoparticles.

2. Experimental procedure

The mechanochemical processing was used for the preparation of nanosized Mn₀.₅Zn₀.₅Fe₂O₄. MnFe₂O₄ and ZnFe₂O₄ were used as starting materials. Details of the mechanosynthesis of Mn₀.₅Zn₀.₅Fe₂O₄ are given in Ref. [10].

\(^{57} \text{Fe} \) Mössbauer spectroscopic measurements were performed in transmission geometry using a \(^{57} \text{Co/Rh} \) \( \gamma \)-ray source. High-field Mössbauer measurements were carried out at 4.2 K in an external magnetic field of 7 T applied parallel to the \( \gamma \)-ray direction. The velocity scale was calibrated relative to \(^{57} \text{Fe} \) in Rh. 'Recoil' spectral analysis software [12] was used for the quantitative evaluation of the Mössbauer spectra. The degree of inversion was calculated from the subspectral intensities (I(2)/I(1)/\( \lambda \)). The average canting angle, \( \psi \), was calculated from the ratio of the intensities of lines 2 and 1, I(2)/I(1), according to \( \psi = 90° - \arcsin(\lambda/2) \).

3. Results and discussions

The low-temperature (4.2 K) Mössbauer spectra of mechanosynthesized Mn₀.₅Zn₀.₅Fe₂O₄, taken in zero applied magnetic fields and in a magnetic field of 7 T applied parallel to the \( \gamma \)-ray direction are compared in Figure 1. As is clearly seen, the thermal fluctuations are suppressed at 4.2 K, and the Mössbauer spectrum of nanocrystalline Mn₀.₅Zn₀.₅Fe₂O₄ consists of sextets only. Although the influence of superparamagnetic relaxation is counteracted, a determination of the cation distribution in Mn₀.₅Zn₀.₅Fe₂O₄ nanoparticles is impossible to make from the low-temperature spectrum at \( H_{\text{ext}} = 0 \) T (figure
I) because it is difficult to resolve the subspectra to assign them to the respective lattice sites. In the presence of an external magnetic field of \(H_{\text{ext}} = 7\ T\), the effective magnetization of the individual particles is aligned along the field. As a consequence of the antiparallel alignment of the spins of \(\text{Fe}^{3+}\) cations in tetrahedral (A) and octahedral [B] coordination of oxygen ions, respectively.

![Figure 1. Low-temperature (4.2 K) Mössbauer spectra of nanosized mechanosynthesized Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) taken (a) in zero applied magnetic field and (b) in external magnetic field of 7 T applied parallel to the γ-ray direction. Blue and red subspectra correspond to \(\text{Fe}^{3+}\) cations in tetrahedral (A) and octahedral [B] sites in spinel ferrites, the external field adds to the magnetic hyperfine field at (A) sites and subtracts from the hyperfine field at [B] sites [6]. Because of this fact, the high-field Mössbauer spectrum of nanosized mechanosynthesized Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) exhibits the completely resolved (A) and [B] subspectra (see figure 1 (b)). Thus, the use of the large external magnetic fields creates an effective separation of the subpatterns, thereby allowing for an accurate determination of the cation distribution. The hyperfine parameters of (A) and [B]-site ferric ions resulting from the least-squares fitting of the spectrum of nanosized Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) are presented in Table 1. The degree of inversion of the mechanosynthesized Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) was found to be \(\lambda = 0.555(4)\).

If the external magnetic field \(H_{\text{ext}}\) is applied parallel to the γ-ray direction, the second and fifth lines of the six-line Mössbauer spectrum vanish for fully collinear magnetic structures [2]. However, figure 1 (b) indicates that in the present study the intensity ratio of the second (or fifth) line to the first (or sixth) line, \(I_{2,5}/I_{1,6}\), takes small values for both (A) and [B] subspectra. This implies that Fe-spins in the (A) and [B] sites of the mechanosynthesized material are strongly canted under the applied field. The obtained intensity ratios \(I_{2,5}/I_{1,6}\) for each subspectrum are also listed in Table 1. The average canting angles, characterizing noncollinear spin arrangement of \(\text{Fe}^{3+}\) ions on (A) and [B] sites in the mechanosynthesized ferrite, were found to be \(\Psi(A) = 22.6(5)^\circ\) and \(\Psi(B) = 24.0(7)^\circ\), respectively. Thus, the spins located on the two sublattices in the mechanosynthesized material are found to behave slightly different in the external field of 7 T. This result is also consistent with previous works, where different spin canting in the (A) and [B] sublattices of spinel nanostructures was observed [14-17].

The effective magnetic fields \(H_{\text{eff}(A)}\) and \(H_{\text{eff}(B)}\) observed at the \(^{57}\text{Fe}\) nuclei in (A) and (B) sites of mechanosynthesized Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\), respectively, are listed in Table 1. Note that the effective magnetic field is the vector sum of the magnetic hyperfine field \(H\) and the applied field \(H_{\text{ext}}\) [18]. The values of the magnetic hyperfine field (listed in Table 1) were estimated from those of the effective magnetic field and external magnetic field using the relationship

\[
H^2 = H_{\text{eff}}^2 + H_{\text{ext}}^2 \pm 2H_{\text{eff}}H_{\text{ext}} \cos \Psi
\]

where \(-\) and \(+\) are for (A) and [B] spectral components, respectively. It is found that the magnetic hyperfine fields experienced by \(\text{Fe}^{3+}\) ions located in the (A) and [B] sites of the mechanosynthesized material are very similar (\(H(A) = 48.91(2)\ T\) and \(H(B) = 49.37(7)\ T\)); thus, it would be impossible to resolve the (A) and [B] subspectra even at low temperatures without application of an external magnetic field (see also figure 1 (a)).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(\text{Fe}^{3+}(\text{A}))</th>
<th>(\text{Fe}^{3+}(\text{B}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>IS (mm/s)</td>
<td>0.262(1)</td>
<td>0.369(5)</td>
</tr>
<tr>
<td>(I(%))</td>
<td>27.77(7)</td>
<td>72.23(7)</td>
</tr>
<tr>
<td>(I_{2,5}/I_{1,6})</td>
<td>0.106(9)</td>
<td>0.120(8)</td>
</tr>
<tr>
<td>(\Psi(\circ))</td>
<td>22.6(5)</td>
<td>24.0(7)</td>
</tr>
<tr>
<td>(H_{\text{eff}}(T))</td>
<td>55.30(4)</td>
<td>42.90(1)</td>
</tr>
<tr>
<td>(H(T))</td>
<td>48.91(2)</td>
<td>49.37(7)</td>
</tr>
</tbody>
</table>

Based on the quantitative results of the low-temperature in-field \(^{57}\text{Fe}\) Mössbauer measurements, it can be stated that the atomic and spin configurations in the mechanosynthesized Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) are characterized by a nonequilibrium cation distribution and noncollinear spin alignment, respectively. Taking into account that \(\text{Zn}^{2+}\) ions have a strong preference for (A) sites in spinels [19], the crystal chemical formula of the mechanosynthesized ferrite can therefore be written as \((\text{Zn}_{0.44}\text{Fe}_{0.56})\text{Fe}_{2}\text{O}_{4}\). Compared with the core–shell configuration of mechanosynthesized
complex oxides [20-22], it can be assumed that both nonequilibrium cation distribution and canted spins are located in the surface shell regions of the \( \text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_{2}\text{O}_{4} \) nanoparticles. Note that the cation distribution in the bulk Mn-Zn ferrite can be described by the following crystal chemical formula: 

\( \text{(Zn}_{x}\text{Mn}_{y}\text{Fe}_{2})\text{O}_{4} \).

The quantitative information on the ion configuration and the spin structure, obtained from the analysis of Mössbauer spectra, is very helpful in the interpretation of both the reduced saturation magnetization \( M_s \) and the enhanced \( N\)éel temperature \( T_N \) of mechanosynthesized Mn-Zn ferrite. Since \( \text{Zn}^2+ \) ions possess no magnetic moment, the total magnetic moment \( \mu \) in \( \text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_{2}\text{O}_{4} \equiv \text{(Zn}_{x}\text{Mn}_{y}\text{Fe}_{2})\text{O}_{4} \) is entirely due to the uncompensated magnetic moments of \( \text{Fe}^{3+} \) and \( \text{Mn}^{2+} \) ions. Thus, from the \( \lambda \) and \( \Psi \) values, the effective magnetic moment (per formula unit) of \( \text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_{2}\text{O}_{4} \) can be calculated as:

\[
\mu = \mu_{\text{Fe}} - \mu_{\text{Mn}} = [(2 - \lambda) \mu_{\text{Fe}} \cos \Psi_{\text{Fe}} + (0.5 - \gamma) \mu_{\text{Mn}} \cos \Psi_{\text{Mn}}] + \lambda \mu_{\text{Fe}} \cos \Psi_{\text{Fe(Mn)}} + y \mu_{\text{Mn}} \cos \Psi_{\text{Mn(Mn)}}
\]

where \( \mu_{\text{Fe}} \) and \( \mu_{\text{Mn}} \) are magnetic moments of \( \text{Fe}^{3+} \) and \( \text{Mn}^{2+} \) ions, respectively: \( \mu_{\text{Fe}} = \mu_{\text{Mn}} = 5 \mu_B \). The values \( \lambda = 0, x = 0.5, y = 0.5, \) and \( \Psi_{\text{Fe}} = \Psi_{\text{Mn}} = 0^\circ \), characteristic of the bulk Mn-Zn ferrite [23], result in the magnetic moment \( \mu_{\text{bulk}} = 7.50 \mu_B/\text{f.u.} \). On the other hand, the values \( \lambda = 0.56, x = 0.44, y = 0, \) and \( \Psi_{\text{Fe}} = 22.6^\circ, \Psi_{\text{Mn}} = 24.0^\circ \) (the same canting angles are assumed for \( \text{Fe}^{3+} \) and \( \text{Mn}^{2+} \) spins in [B] sites), characteristic of the mechanosynthesized material, lead to the effective magnetic moment \( \mu_{\text{anno}} = 6.28 \mu_B/\text{f.u.} \), characteristic of the surface shell regions of the noncollinear spin effects in the surface shell of \( \text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_{2}\text{O}_{4} \). Since \( \text{Zn}^2+ \) ions possess no magnetic moment, the total magnetic moment \( \mu \) in \( \text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_{2}\text{O}_{4} \equiv \text{(Zn}_{x}\text{Mn}_{y}\text{Fe}_{2})\text{O}_{4} \) is entirely due to the uncompensated magnetic moments of \( \text{Fe}^{3+} \) and \( \text{Mn}^{2+} \) ions. Thus, from the \( \lambda \) and \( \Psi \) values, the effective magnetic moment (per formula unit) of \( \text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_{2}\text{O}_{4} \) can be calculated as:

\[
\mu = \mu_{\text{Fe}} - \mu_{\text{Mn}} = [(2 - \lambda) \mu_{\text{Fe}} \cos \Psi_{\text{Fe}} + (0.5 - \gamma) \mu_{\text{Mn}} \cos \Psi_{\text{Mn}}] + \lambda \mu_{\text{Fe}} \cos \Psi_{\text{Fe(Mn)}} + y \mu_{\text{Mn}} \cos \Psi_{\text{Mn(Mn)}}
\]

where \( \mu_{\text{Fe}} \) and \( \mu_{\text{Mn}} \) are magnetic moments of \( \text{Fe}^{3+} \) and \( \text{Mn}^{2+} \) ions, respectively: \( \mu_{\text{Fe}} = \mu_{\text{Mn}} = 5 \mu_B \). The values \( \lambda = 0, x = 0.5, y = 0.5, \) and \( \Psi_{\text{Fe}} = \Psi_{\text{Mn}} = 0^\circ \), characteristic of the bulk Mn-Zn ferrite [23], result in the magnetic moment \( \mu_{\text{bulk}} = 7.50 \mu_B/\text{f.u.} \). On the other hand, the values \( \lambda = 0.56, x = 0.44, y = 0, \) and \( \Psi_{\text{Fe}} = 22.6^\circ, \Psi_{\text{Mn}} = 24.0^\circ \) (the same canting angles are assumed for \( \text{Fe}^{3+} \) and \( \text{Mn}^{2+} \) spins in [B] sites), characteristic of the mechanosynthesized material, lead to the effective magnetic moment \( \mu_{\text{anno}} = 6.28 \mu_B/\text{f.u.} \). Thus, the disordered cation and spin configurations theoretically lead to the \( M_s \) value that is approximately 1.2 times smaller than that of the ordered bulk material. This is in reasonable agreement with the results of magnetization measurements, which demonstrate that Ms of mechanosynthesized Mn-Zn ferrite is about 1.7 times smaller than that calculated for the bulk material. Thus, the theoretical considerations presented above clearly demonstrate that the origin of the reduced Ms of mechanosynthesized Mn-Zn ferrite lies in both nonequilibrium cation distribution and spin disorder. Compared with other mechanosynthesized spinel ferrites, the magnetic degradation observed in the present case can be attributed to the nonequilibrium cation and noncollinear spin effects in the surface shell of \( \text{Mn}_{0.6}\text{Zn}_{0.4}\text{Fe}_{2}\text{O}_{4} \) nanoparticles [20, 21].

Taking into account the crystal chemical formulas of \( \text{(Zn}_{x}\text{Mn}_{y}\text{Fe}_{2})\text{O}_{4} \) and \( \text{(Zn}_{0.6}\text{Fe}_{0.5})\text{O}_{4} \), characteristic of bulk and nanocrystalline Mn-Zn ferrites, respectively, it is evident that the mechanosynthesized ferrite possesses a larger number of the (A)-O-[B] exchange paths. This is directly related to the \( N\)éel temperature of the ferrite system [14]. The enhanced \( T_N \) observed for the mechanosynthesized material can therefore be attributed to the strengthening of the (A)-O-[B] superexchange interaction due to an increase of the magnetic ion concentration in the (A) site [24-25].

4. Conclusions

A low temperature in-field \( ^{57}\text{Fe} \) Mössbauer spectroscopy has proved a powerful technique for the elucidation of atomic local structure in MnZn nanoferrite and of the changes in their cation distributions brought about by mechanical activation. Based on Mössbauer spectroscopy results, the reduced saturation magnetization in respect to the bulk sample is due to nonequilibrium cation distribution and spin disorder. The enhanced Curie temperature of MnZn nanoferrite compared with bulk sample can be attributed to the strengthening of the (A)-O-[B] superexchange interactions due to an increase of the magnetic ion concentration in the (A) site.

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References