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Mössbauer study of Mn–Zn spinel ferrites prepared by a wet chemical method

M. PETRERA, A. GENNARO, N. BURRIESCI
Instituto G. Donegani S. p. A., Novara, Italy

The γ-ray resonance technique has been employed for the study of the magnetic structure of a series of Mn--Zn ferrites, prepared by a wet chemical method, before and after high-temperature annealing. In agreement with previously reported results, ionic spin relaxation has been observed for the annealed sample $Mn_{0.4}Zn_{0.6}Fe_2O_4$. On the other hand, the unannealed sample with the same concentration has shown the existence of superparamagnetic clusters, as proposed by Ishikawa, which exist simultaneously with ferrimagnetic regions in the material. These findings are explained in terms of the magnetic disorder resulting from the particular method of preparation.

1. Introduction

Ferrites with spinel structure, such as Ni–Zn, Co–Zn, Li and Co ferrites, have been the subject of many studies because of their magnetic properties resulting from a particular configuration of the cations in the lattice. Relatively easy preparation and low cost make these materials widely usable for cores of intermediate- and high-frequency transformers, inductors, loudspeakers and other electromagnetic devices [1]. The usual ceramic preparation of ferrites proceeds through a high-temperature reaction between finely-milled oxide (or carbonate) powders followed by shaping by successive pressing and sintering.

Materials of the same composition, but with very different properties can be prepared at lower temperatures as wet ferrites by co-precipitation from aqueous solutions of the corresponding hydroxides [2].

With the exception of a few works [1, 3] wet-prepared ferrites have, however, not been extensively studied and only in recent years have comparative studies on ceramic and wet ferrites appeared in the literature for $Co_{1-y}Fe_{2+y}O_4$ [4] and $Zn_xMn_{1-x}Fe_2O_4$ [5, 6].

Mixed Mn–Zn ferrites can be prepared by the wet method over a very large range of composition between manganese and zinc ferrite [5]. They are characterized by anomalous electrical and magnetic properties and are highly reactive and can therefore sinter at much lower temperatures than the ferrites prepared by the ceramic method [3]. Moreover, when heated at sufficiently high temperatures (~ 1300° C), the properties of the wet materials become more similar to those obtained with the usual ceramic preparation [5, 6]. These peculiar properties have been ascribed to a structural disorder caused by a different cation distribution within the lattice sites of the wet-prepared materials.

The disorder is reduced by suitable thermal treatments [6], as demonstrated by Mössbauer spectroscopy measurements. This technique, and the neutron diffraction technique, can be of great aid in the study of the magnetic structure of these mixed spinel ferrites.

Recently, the complex magnetic structure of Co–Zn [7], Ni–Zn [8] and Mn–Zn [9] ferrites prepared by the ceramic method has been elucidated employing high-field Mössbauer spectroscopy.

In a previous study [6], γ-ray resonant absorption measurements have been used for the determination of the cation distribution in wet-prepared Mn–Zn ferrites of the type

$$(Zn_xMn_yFe_{1-x-y})[Mn_{1-x-y}Fe_{1+x+y}]O_4$$

with $x \leqslant 0.3$, where round and square brackets refer to ions occupying, respectively, tetrahedral and octahedral sites in the spinel lattice. In the present work, a discussion of the magnetic struc-

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ture of the wet-prepared materials derived from the Mössbauer spectra is given and the influence of successive annealing is considered. Particular attention has been devoted to the zinc-rich region ($x \geqslant 0.4$ of the ferrite system, where the most pronounced difference between the co-precipitated and ceramic materials is observed.

2. Experimental procedure

Variable composition Mn–Zn ferrites were prepared [5] by slowly adding solutions of $FeSO_4 \cdot 7H_2O$, $MnSO_4 \cdot H_2O$, $ZnSO_4 \cdot 7H_2O$ and NaOH in water while stirring and bubbling air. Temperatures varied between 60 and 90° C and a pH value of 9.5 was maintained. All samples were filtered, washed and dried at 100° C under vacuum. Eight compositions have been prepared in the range $0.0 \leqslant x \leqslant 0.8$. These samples (Samples W) have an average particle size of 0.12 to 0.13 μm and a specific surface area of 5 to 9 $m^2\ g^{-1}$.

The annealed samples (Samples Q) were obtained from the samples of the W-series by heating them at 1350° C in a P_{O_2} atmosphere for 2 to 6 h and then quenching in cold water. X-ray structural analysis shows that all samples are single-phase with spinel structure and lattice constant between 0.845 and 0.852 nm. No amorphous phase has been detected. The magnetic measurements were carried out with a PAR magnetometer in an external magnetic field of 1.8 T.

The Mössbauer spectra were recorded in the constant acceleration mode using a ^{57}Co/Rh source. Two spectrometers (Elscint AME 40 C and Laben 8100) were alternately employed. Low-temperature measurements were carried out in a liquid-nitrogen Oxford Instruments Mössbauer cryostat. Spectra were also collected in applied, transverse magnetic fields of 1.2 and 5.0 T, respectively, at 290 and 4.2 K. The lower magnetic field was obtained using a conventional electromagnet and the higher field was produced by means of a Thor superconducting magnet.

A least-square fit computer program with Lorentzian components was used to determine the Mössbauer parameters. Where many hyperfine fields are present, the minimum number of sextets was assumed in order to obtain an acceptable value for the quality-of-fit parameter, χ^2.

3. Results and discussion

3. 1. Magnetic structure

In mixed ferrites containing Zn the saturation magnetization is known to increase linearly (following the theory of Néel) for Zn concentrations up to about 50 at% and to decrease thereafter with increasing Zn content [10, 11].

Such a different behaviour with respect to the theory of Néel has been tentatively explained in various ways. The partial oxidation of Mn^{2+} to Mn^{3+} and a formation of $Fe^{2+} - Mn^{3+}$ pairs with consequent lowering of the magnetic moment has been proposed [12, 13], but Mössbauer measurements [9, 10, 14] and theoretical calculations [15] definitely rule out this possibility. Neutron diffraction [16] and Mössbauer measurements on Ni–Zn ferrites [11] and $MnFe_2O_4$ [14, 17] led to the conclusion that their magnetic structure is explained by a non-collinear arrangement of spins, following the Yafet–Kittel model [18]. It can be shown that this spin arrangement is energetically possible [5, 14]. On the other hand, this canted spin hypothesis is in disagreement with some experimental data on Mn–Zn ferrites which seem to indicate that the spins of the various cations are collinear to the [1 1 1] direction of the elementary cell, at least for Zn-concentrations up to 0.4 [10, 19]. The same conclusion was reached in the case of the Ni–Zn ferrites for Zn-concentrations up to 0.4 [11].

One further hypothesis for the explanation of the low magnetic moments of these materials introduces covalency effects due to electronic orbital superposition and overlap distortion of the spin densities [14]. This gives rise to a new contribution to the hyperfine magnetic field besides that given by the superexchange interactions [20]. A reduction in the magnetic moments of the metallic ions arises from a spin-density delocalization related to the influence of the neighbouring anion orbitals.

The relevance of covalency effects can be argued from a comparison between the ionic radii of tetrahedral or octahedral sites, which are related to the oxygen, u, and cell, a, parameters of the spinel lattice [21]. This comparison indicates a strong superposition of the electronic orbitals which accounts for the lower values of the saturation magnetization at 0 K, relative to those expected for a collinear spin arrangement.

In the particular case considered in this work samples of the W-series are characterized by smaller lattice constants than are those of the Q-series [6]. Therefore, due to stronger covalency effects arising from smaller cationic site dimensions, Samples W are expected to have a lower saturation magnetization with respect to Samples Q, in accordance with the experimental evidence (see Fig. 1).

For the explanation of the behaviour of these materials following the progressive introduction of a diamagnetic ion, their magnetic structure should be analysed in greater detail.

The strong preference of Zn^{2+} ions for tetrahedral positions is well known [10]. Considering that in spinels the A–A and B–B superexchange interactions are negligible in first approximation with respect to the dominant A–B interactions [10, 19], the presence of zinc will predominantly influence the hyperfine magnetic fields acting on B-ions and will only indirectly influence those acting on A-ions.

However, it is a common occurence in spinel ferrites that no distribution in the values of hyperfine field is observed for any variation of the surrounding in the case of tetrahedral iron, whereas a large distribution is present for octahedral iron even in the absence of diamagnetic ions (i.e., $x = 0$).

There is experimental evidence that the substitution of only one Fe^{3+} ion with one Mn^{2+} ion, having the same magnetic moment of $5\,\mu_B$, where μ_B is the Bohr magneton, causes a change of more than 1.0 T in the hyperfine field acting on octahedral site iron [14]. The fact that such variations are not observed for tetrahedral iron seems rather surprising.

As can be seen from Fig. 2, the only difference between the two situations is that six oxygen atoms (one for each A-neighbour of a B-site) take part in the supertransferred interaction toward a B-ion, while only four oxygen atoms (one for every three B-neighbours of an A-site) contribute to the magnetic field transfer toward an A-ion. This means that a variation comparable to the substitution with Mn of an A-site Fe in manganese ferrite could be obtained only with the substitution with Mn of all the three B-site Fe ions transferring their magnetic field through the same oxygen ion. The negligible probability of this kind of arrangement, due also to the low concentration of octahedral manganese, accounts for the absence of any distribution in the hyperfine field value for tetrahedral iron.

The dependence of the 0 K saturation magnetization on the Zn concentration, x, has been investigated already in the previous paper [6] for wet-prepared Mn–Zn ferrrites in comparison with analogous annealed and ceramic ferrites. It has been shown there that for low x-values the saturation magnetization, $m\,(0,x)$ curves can well be explained on the basis of the different inversion degrees, λ,

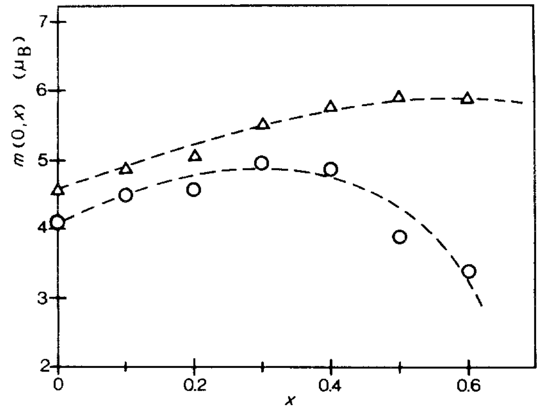

Figure 1 Extrapolated saturation magnetization at 0 K plotted against Zn-concentration. (○) Samples W; (△) Samples Q.

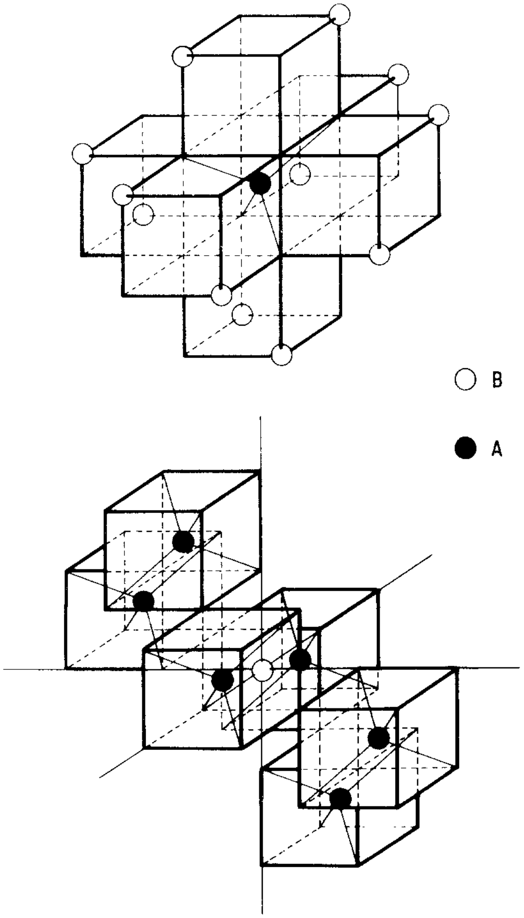

Figure 2 Configuration of the nearest nieghbours of the tetrahedral (A) and octahedral (B) cationic sites in a spinel crystal lattice. All corners not occupied by octahedral cations represent oxygen positions.

which decrease for increasing Zn-concentration according to the tendency towards formation of a normal spinel, like $ZnFe_2O_4$. The progressive disappearance of tetrahedral iron gives rise to the observed increase of m (0, x) in the range of x from 0 to about 0.5, as a consequence of the reduced compensation of tetrahedral sublattice magnetization.

Moreover, the wet-prepared samples have a higher inversion degree than the annealed and quenched samples. This means that a redistribution of the cations takes place for low Zn-concentrations during the thermal treatment, whereas a similar situation to the ceramic-prepared samples is obtained after quenching of the wet-prepared samples from temperatures above 1300° C. The low-temperature preparation evidently gives rise to a lower degree of magnetic ordering than that typical of these compounds at the thermodynamical equilibrium. As a consequence, the lower values of m (0, x) and, in general, the less-exciting magnetic properties of the wet-prepared samples are accounted for in the range $x \leqslant 0.3$.

As already pointed out before, all mixed ferrites containing Zn are characterized by a drop of the saturation magnetization for x-values greater than about 0.4 to 0.5 (see Fig. 1). By means of high-field Mössbauer spectroscopy measurements, several authors [7, 8, 10] found that at high zinc concentrations the magnetic moments of iron ions are non-collinear and some Fe-ions on B-sites have reversed magnetic moments with respect to the normal B-sublattice magnetization. A magnetic moment reversal is most likely when the octahedral iron has all six A-site nearest neighbours occupied by diamagnetic Zn-ions [10]. Moreover, in the case of wet-prepared Mn–Zn ferrites fired at 1300° C, tetrahedral Fe is known to be absent in the Zn-rich region [10]. On the basis of our previously reported Mössbauer investigation [6], the same situation is thought to be typical also of the wet-prepared and of the annealed ferrites.

The observed difference in $m(0x)$ between the last two series of samples for $x \geqslant 0.4$ could therefore be explained either in terms of a different fraction of octahedral Fe^{3+} ions with reversed magnetic moments or in terms of a different degree of canting of the magnetic moments.

3.2. Mössbauer characterization

Bearing in mind these general features of Zn-containing mixed ferrites, let us now examine our room-temperature (RT) and liquid-nitrogen-temperature (LNT) Mössbauer spectra, reported in Fig. 3 and 4, respectively.

Whereas, at low Zn-content, for both series, no substantial difference was observed between RT and LNT spectra [6], a more complicated situation seems to be present in the case of $x \geqslant 0.4$. Considering at first the samples of the Q-series, the pro-

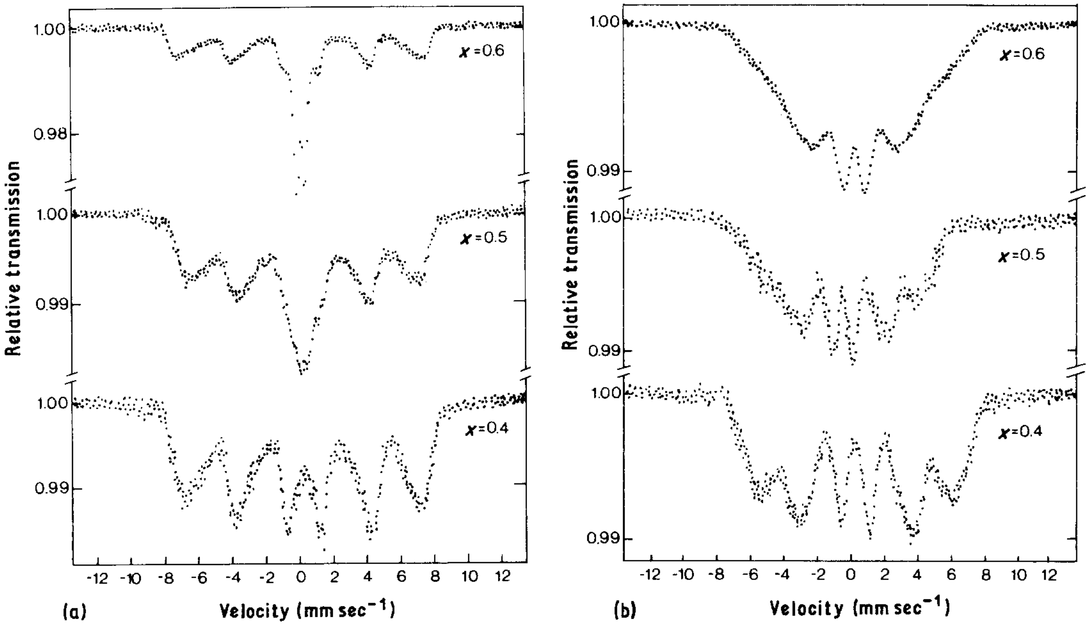

Figure 3 Mössbauer spectra at RT of the samples of (a) the W-series and (b) the Q-series with $x \geqslant 0.4$.

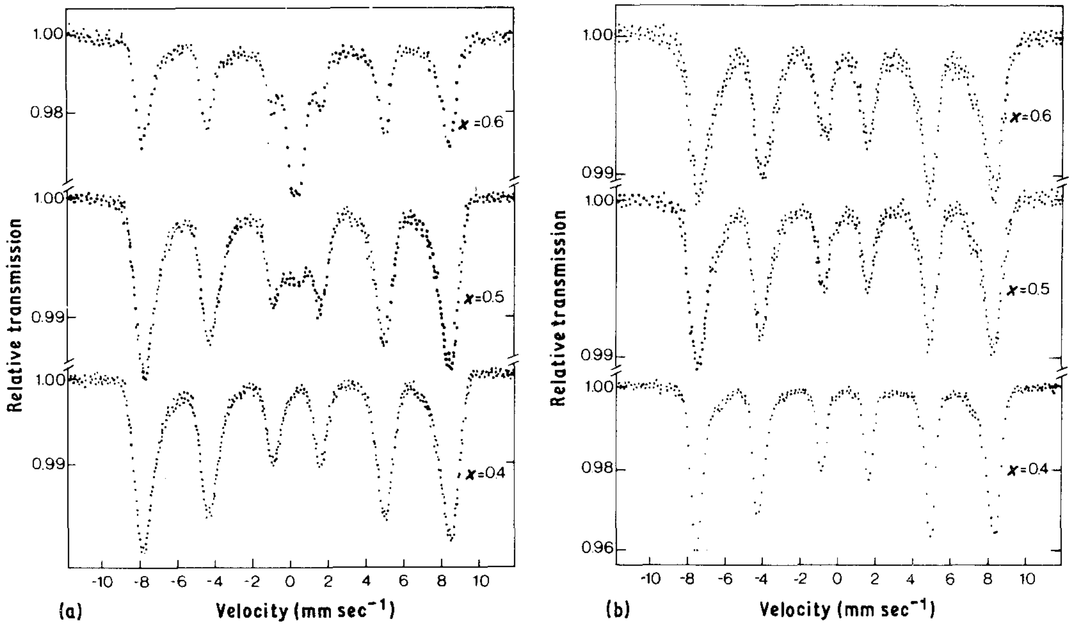

Figure 4 Mössbauer spectra at LNT of the samples of (a) the W-series and (b) the Q-series with $x \geqslant 0.4$.

gressive introduction of diamagnetic ions in the spinel lattice gives rise to an increasing broadening of the resoance lines at RT. The resulting superposition of six-line patterns is well resolved in the low-temperature spectra. By comparison with the analogous system of mixed Ni–Zn ferrites prepared by a ceramic method [24, 25] or by a wet method followed by firing at 1200° C [11] an explanation of the features of the RT spectra which takes into account the presence of ionic spin-relaxation phenomena causing rapid fluctuation of the magnetization is expected.

Mössbauer measurements were made at variable temperatures on the sample of the Q-series with $x = 0.6$ in order to clarify this point. The corresponding spectra are shown in Fig. 5. The temperature-dependence of the relative line positions Δ_{16}/Δ_{34} and Δ_{25}/Δ_{34} has been reported in Fig. 6. As in absence of fluctuation effects these ratios are independent of temperature [24, 26], the observed variations clearly show the presence of spin-relaxation phenomena, in agreement with the results obtained on ceramic Mn–Zn ferrites [26]. Let us now consider the Mössbauer spectra of the W-series samples with $x \geqslant 0.5$. They are characterized by the presence of a central doublet which increases for increasing Zn-content with respect to the magnetically-split component which exhibits a small temperature-dependence of the hyperfine splitting. The appearance of a paramagnetic contribution in the Mössbauer spectra of the wet-prepared samples agrees with their particularly low saturation magnetization and can be attributed to the presence of either superparamagnetic particles or paramagnetic centres for Fe^{3+}.

Mössbauer spectra taken at different temperatures of the $x = 0.6$ sample of the W-series are reported in Fig. 7. Fig. 8. shows the temperature-dependence of the magnetic-to-paramagnetic area ratio, indicating a pronounced superparamagnetic behaviour. The area ratios were calculated from a computer fitting introducing two six-line patterns and a central doublet. The values obtained for the hyperfine splitting for the two magnetic components range from 50.3 and 46.8 T at 80 K to 45.6 and 40.0 T at 291 K, respectively. Standard deviations of the order of 0.2 T are estimated.

The magnetic relaxation is not completely removed either by a decrease of the temperature down to LNT, or by the application of an external transverse magnetic field of 1.2 T (see Fig. 9a). A complete ordering of the magnetic moments in the spinel structure is achieved only at a temperature of 4.2 K (LHT) in the presence of an applied transversal magnetic field of 5.0 T, as shown in Fig. 9b.

A similar and even more marked behaviour was observed for a wet-prepared sample with $x = 0.8$, whose Mössbauer spectra in different conditions are shown in Fig. 10. For this sample, the para-

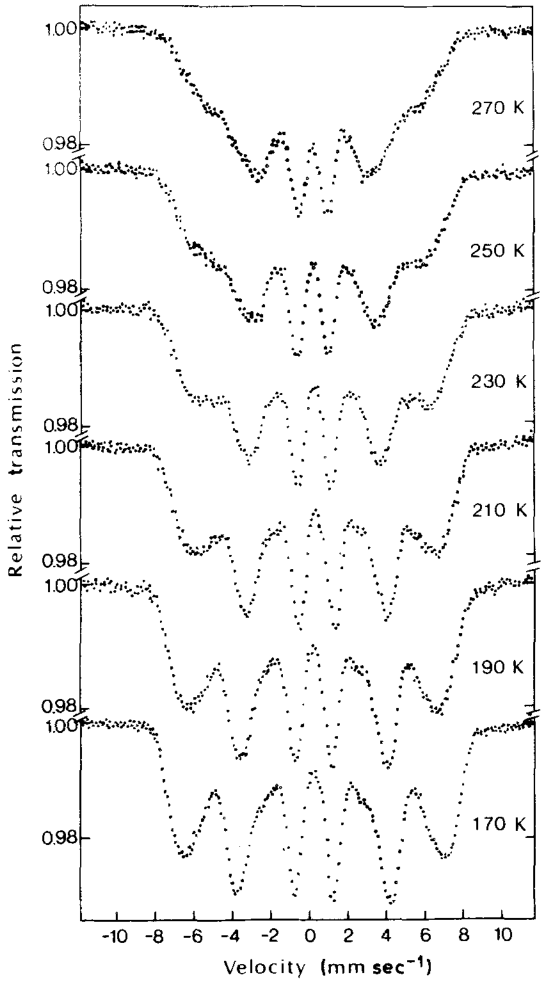

Figure 5 Temperature-dependence of the Mössbauer spectra for the $x = 0.6$ sample for the Q-series.

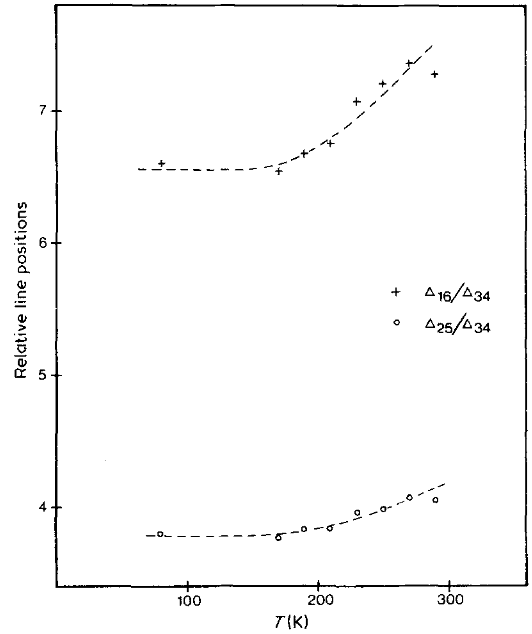

Figure 6 Temperature-dependence of the relative line positions for the $x = 0.6$ sample of the Q-series derived from the spectra in Fig. 5.

magnetic component is transformed at LHT and in the external paramagnetic field of 5.0 T into a relaxed spectrum indicating the partial transition to an ordered magnetic structure.

We are thus led to the conclusion that, in the high zinc-content co-precipitated samples a large fraction of the superparamagnetic particles have a very small size or, more probably, that instead of ferrimagnetic fine particles in this case there are ferrimagnetic regions separated magnetically from the matrix, since the region is surrounded by non-magnetic Zn-ions. The same conclusion was reached by Ishikawa [27] for the explanation of the superparamagnetic behaviour found in magnetically-dilute systems, like $Zn_{0.9}Ni_{0.1}Fe_2O_4$.

The observation of the LHT spectra recorded in the 5.0 T external magnetic field indicates that an antiferromagnetic coupling is also present in samples of the W-series with x = 0.6 and 0.8 between two sublattices with opposed magnetizations.

By comparison with the spectra reported by Morrish *et al.* [10], the innermost magnetic pattern of the spectra in Figs. 9b and 10d is attributed to octahedral iron, whereas the outermost pattern is to be attributed to octahedral iron ions with reversed magnetic moments. Referring to the spectrum of Fig. 9b the following remarks should be added:

(a) The relative amount of B-site iron ions with reversed magnetic moments is about 30%. As the reported value for a ceramic sample with $x = 0.6$ is about 8.5% [10], our wet-prepared sample shows a cation distribution like that of a ceramic sample with an higher x-value; (b) No new magnetic component is generated by the magnetic ordering of the iron ions which are paramagnetic at RT. As the relative amount of paramagnetic iron to total iron is about 60% at RT (see Fig. 8), it is deduced that after ordering, the ferrimagnetic fine particles probably contribute to the saturation magnetization of both octahedral mangetic sublattices.

4. Conclusions

It is apparent from the reported results that the different magnetic properties of the wet-prepared

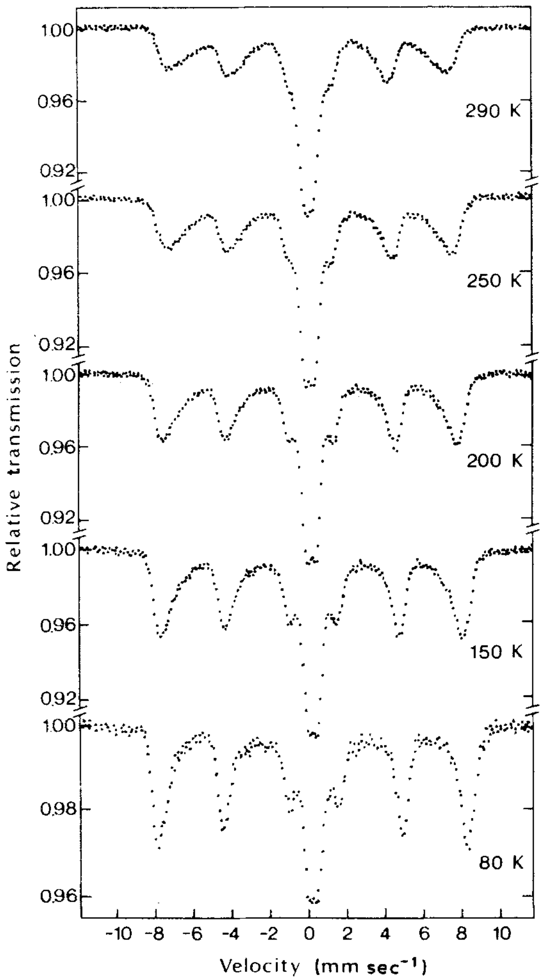

Figure 7 Temperature dependence of the Mössbauer spectra for the $x = 0.6$ sample of the W-series.

ferrites with respect to the ceramic and annealed ones cannot be attributed simply, for the high zinc-content samples, to a different cation distribution between the magnetic sublattices, affected by an increasing ionic spin relaxation for increasing concentration of the diamagnetic ions. The reported Mössbauer spectra clearly indicate that, in the case of the wet-prepared ferrites, magnetically-ordered regions, superparamagnetic clusters and paramagnetic centres are simultaneously present, contrary to what is observed for the annealed and quenched ferrites, which closely resemble the ceramic ferrites in terms of their magnetic relaxation behaviour.

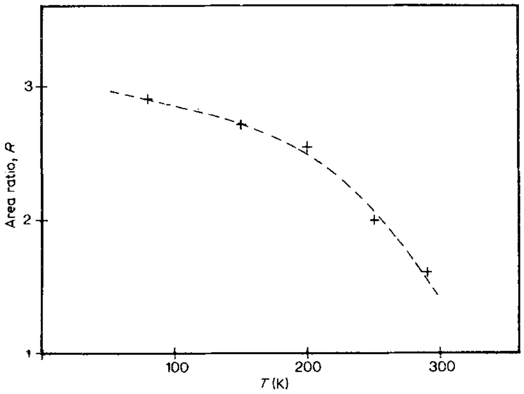

Figure 8 Temperature-dependence of the magnetic-to-paramagnetic area ratio, R, as derived from the spectra in Fig. 7.

The lower values of the extrapolated saturation magnetization are therefore due to the fact that the clusters with smaller size are not saturated by the 1.8 T external field at the temperature of the magnetic measurements. It is believed that these results are related to the preparation conditions. The low temperature of synthesis of the wet-prepared ferrites leads to highly-disordered systems characterized by local concentrations of diamagnetic zinc ions, which hinder the propagation of the inter-sublattice supertransferred hyperfine interactions. The successive annealing and quenching apparently bring the samples back to the ordered magnetic structure of the ceramic ferrites. In this case the tetrahedral magnetic cation (Mn^{2+}) concentration for the investigated composition range ensures magnetic ordering through the entire crystal at much higher temperatures than for the wet-prepared samples, due to the completely random and uniform distribution of magnetic A-sites.

Another observation which can be made from the reported Mössbauer spectra is that the ionic

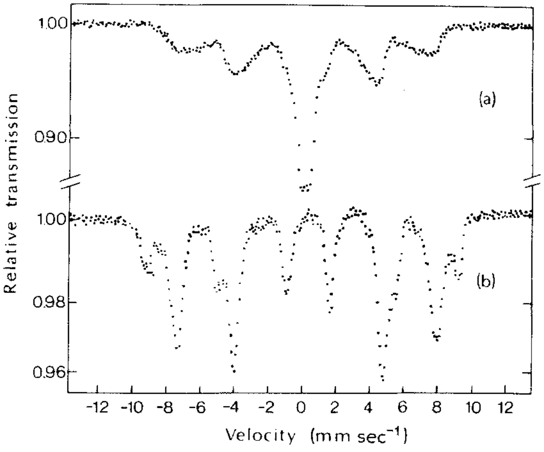

Figure 9 Mössbauer spectra in a transverse magnetic field of the $x = 0.6$ sample of the W-series (a) in 1.2 T at RT; (b) in 5.0 T at LHT.

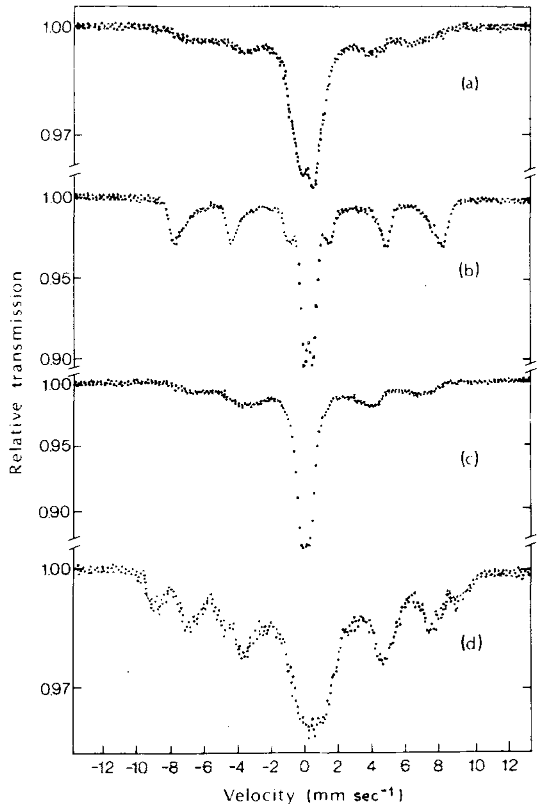

Figure 10 Mössbauer spectra of the $x = 0.8$ sample of the W-series (a) at RT; (b) at LNT; (c) in 1.2 T transverse magnetic field at RT; (d) in 5.0 T transverse magnetic field at LHT.

spin-relaxation of the magnetically-ordered regions seems to be hampered by the presence of the magnetically-isolated clusters.

We therefore conclude that the samples of the W-series for high zinc concentrations are not to be considered as a true solid solution, but rather as constituted locally of paramagnetic regions with composition, close to zinc ferrite and ferrimagnetic regions with mixed ferrite composition and x-values lower than the reported average value.

Finally, the Ishikawa model, which was found not to be applicable to the Ni–Zn ferrite system, has to be accepted to account for the magnetic properties and the Mössbauer spectra of the wet-prepared Mn–Zn ferrites with $0.5 \leqslant x \leqslant 0.8$.

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