

VARIABLE-TEMPERATURE MÖSSBAUER SPECTROSCOPY OF NANO-SIZED MAGHEMITE AND Al-SUBSTITUTED MAGHEMITES

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Abstract—Synthetic aluminum-substituted maghemite samples, $\gamma\text{-(Fe}_{1-x}\text{Al)}_2\text{O}_3$, have been prepared by thermal decomposition of Al-lepidocrocite ($\gamma\text{-Fe}_{1-x}\text{Al}_x\text{OOH}$), with $x = 0, 0.04, 0.06, 0.14$ and 0.18 . The particles are needle-shaped and the mean crystallite diameter along the [311] crystallographic direction was found to be between 2.0 and 5.0 nm. Mössbauer spectra were collected at 6 K and from 80 K up to 475 K at steps of 25 K. In a wide range of temperatures the spectra of the non-substituted sample consist of a superposition of a broad sextet and a superparamagnetic doublet, whereas for the Al-maghemites this range is much smaller. From the temperature variation of the fractional doublet area two different parameters were defined: the temperature corresponding to a 50/50 doublet-sextet spectrum ($T_{1/2}$), and the temperature below which the doublet ceases to exist (T_0). These two parameters ($T_{1/2}$ and T_0) decrease from 390 K and 92 K (Al-free sample), to 118 K and 64 K (4 mole % Al) and to 100 K and 48 K (18 mole % Al), respectively. The average hyperfine fields at 6 K undergo a steep drop in going from the Al-free sample ($\bar{H}_{\text{hf}} = 506$ kOe) to the sample with 4 mole % Al ($\bar{H}_{\text{hf}} = 498$ kOe), but for higher substitutions the effect is much smaller. The A- and B-site quadrupole splittings, obtained from the data between 220 K and 475 K, were found as: $\Delta E_{\text{Q,A}} = 0.86 \pm 0.04$ mm/s and $\Delta E_{\text{Q,B}} = 0.65 \pm 0.04$ mm/s for the 4 mole % Al sample. The characteristic Mössbauer temperature, determined from the temperature dependence of the average isomer shift, was found to be in the range of 500–600 K.

Key Words—Al substitution, Maghemite, Mössbauer effect.

INTRODUCTION

Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is a spinel ferrite, containing only Fe^{3+} cations in both tetrahedral and octahedral lattice sites, the so-called A and B sites respectively. The maghemite structure is unique in the sense that some of the cation lattice sites, which are normally occupied in a spinel compound, are empty (on the average one third per formula unit). The distribution of these vacancies among the A and B sites is not always obvious. For maghemite samples whose X-ray diffraction patterns (XRD) show superstructure lines characteristic for octahedral 1:5 ordering, it is certain that the vacancies are exclusively on B-sites. The appearance of superstructure lines seems to depend on the mean particle size, with no such lines present for nano-sized samples (Haneda and Morrish 1977). In this case, it is possible that the poor crystallinity inhibits the ordering. Another possibility is that part of the vacancies are located on the A sites, and as a result, no 1:5 ordering can exist on the B sites. The X-ray diffraction pattern of small-particle maghemite shows only very broad peaks in the region of the main reflections. As

the superstructure lines are normally much weaker, it cannot be excluded that the line broadening obscures their detection, making it difficult to decide about the exact location of these vacancies.

Aluminum-substituted maghemites are known to be important constituents of many magnetic soils. There are basically three mechanisms that may lead to the formation of maghemite in soils: oxidation of magnetite, conversion of some other iron oxides (e.g., goethite and hematite) by forest fires, and less likely, dehydration of lepidocrocite (Schwertmann 1988). As far as the authors are aware, no quantitative data for the particle sizes of soil maghemites seem to be available in the literature. Nevertheless, considering that the size of most iron oxides in soils ranges from approximately 10 nm to 100 nm, it is likely that maghemite will also be nano-sized. For substituted samples an additional complication arises in that the Al cation can in principle occupy both sites, or may show a certain preference for one particular site. In that respect, it appears that the method used to synthesize the samples plays a role to some extent. For instance, Wolska and Schwertmann (1989) prepared Al-maghemites by coprecipitation of Al and Fe hydroxides and claimed that about 20% of Al is located on the tetrahedral sites. In contrast, Bowen et al (1994) prepared relatively well-

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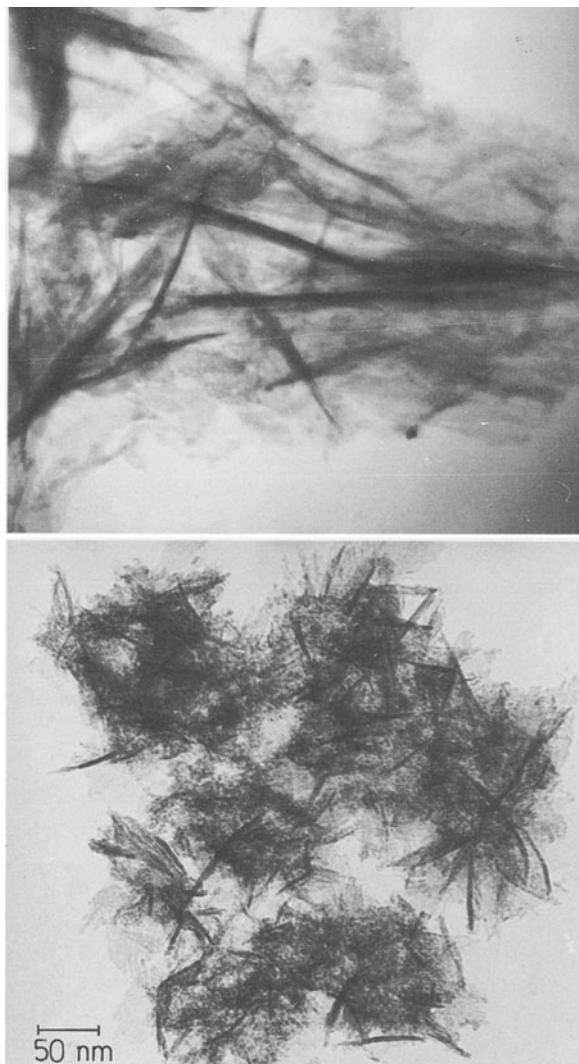


Figure 1. TEM photographs of samples ML0 (top) and ML14 (bottom).

crystallised samples (hereafter referred to as the M samples) from mixtures of Al hematites and sucrose, and concluded that the Al ions occupy B sites only. Furthermore, in a recent preliminary study from our laboratory, dealing with the external-field Mössbauer spectra (MS) of poorly crystalline Al maghemites (hereafter referred to as ML samples) prepared by thermal decomposition of aluminum-substituted lepidocrocites ($\gamma\text{-Fe}_{1-x}\text{Al}_x\text{OOH}$), it has been suggested that the Al ions as well as the vacancies are possibly located on both A and B sites (da Costa *et al* 1994a).

The present paper reports the results of a careful and more complete Mössbauer effect study of the poorly crystalline Al-maghemite samples at variable temperature between 6 K and 475 K. These results are complementary to the results obtained from a similar investigation recently carried out for the more crystalline

M samples (da Costa *et al* 1994b). It is believed that the two data sets will eventually be useful for the characterization of maghemite-containing soils by means of Mössbauer spectroscopy.

EXPERIMENTAL PROCEDURES

Maghemite and Al-substituted maghemite samples were prepared by thermal decomposition at 573 K of lepidocrocites containing different amounts of aluminum ($\gamma\text{-Fe}_{1-x}\text{Al}_x\text{OOH}$, $x = 0, 0.04, 0.06, 0.14$ and 0.18) (Bryan 1993). Samples are code-named as MLX (ML0, ML4, ML6, ML14 and ML18) where X stands for the mole % of Al in the parent lepidocrocites ($X = 100x$). The characterization of the products, using X-ray diffraction, transmission electron microscopy (TEM) and external-field Mössbauer spectroscopy, has been reported in an earlier paper (da Costa *et al* 1994a).

Mössbauer spectra for all samples were collected at 6 K and from 80 K up to 475 K at steps of 25 K. Isomer shifts are quoted relative to metallic iron. More details about the experimental set-up can be found elsewhere (da Costa *et al* 1994c).

RESULTS AND DISCUSSION

The TEM photographs of samples ML0 and ML14 are shown in Figure 1. The particles are needle-shaped, with the smaller axis reaching a few nanometers. Size estimation is not feasible because the particles seem to be grouped together, probably due to the ferrimagnetic character of maghemite. The mean crystallite diameter (MCD) along the [311] crystallographic direction, as estimated from the diffractograms, ranges from 2.0 to 5.0 nm. A correlation between MCD and x could not be observed due to the extremely poor definition of the involved reflection in the XRD patterns.

Mössbauer spectra of samples ML0 and ML6 at some selected temperatures are depicted in Figure 2. The spectral behavior of the other compositions is very similar to that of ML6. At 6 K all five samples with different amounts of Al substitution exhibit an asymmetrical sextet which is characteristic for the presence of a magnetic hyperfine-field distribution (MHFD). The problems associated with the numerical analysis of these spectra have been discussed previously by da Costa *et al* (1994c). These authors concluded that neither the use of two discrete, but constraint Lorentzian-shaped sextets, nor the use of a superposition of two model-independent MHFD, yielded acceptable results for the various Mössbauer parameters. For the purpose of the present investigation, it was therefore decided to fit all 6 K spectra with one single MHFD with adjustable line width Γ of the basic sextet. The quadrupole shift was forced to be zero. Obviously, this approach will not give any information concerning the site occupancy and the obtained hyperfine data will be average values for A- and B-site ferric ions.

As Figure 2 shows, this fitting procedure adequately

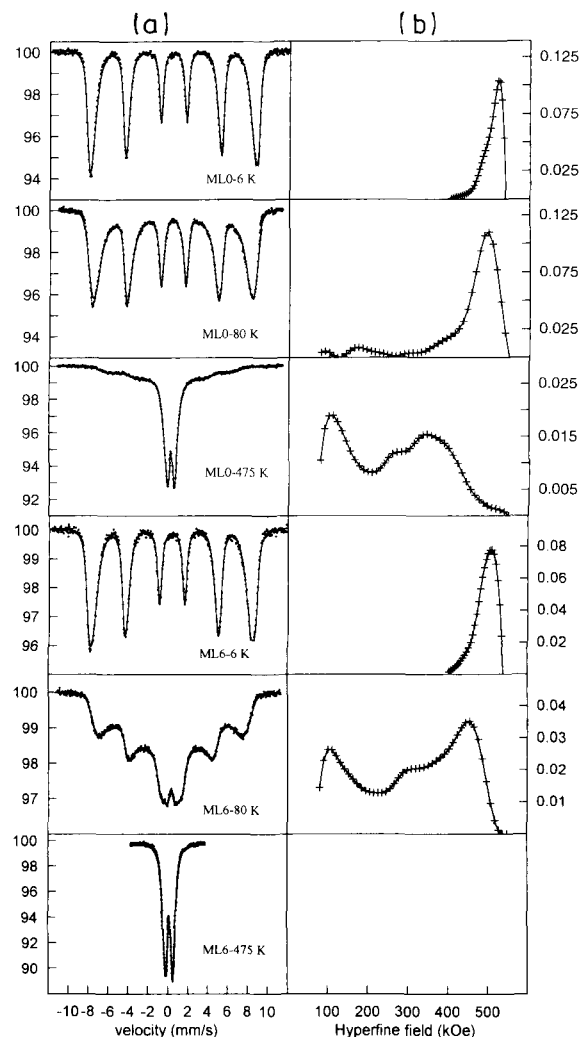


Figure 2. Mössbauer spectra of samples ML0 and ML6 at some selected temperatures (a) and hyperfine-field distributions (b).

describes the observed line shapes of the 6 K spectra. The derived probability distributions, $p(H_{\text{hf}})$, shown to the left of each spectrum, are clearly asymmetric. The relevant numerical results are listed in Table 1. Both the average hyperfine field, \bar{H}_{hf} , and the maximum-probability field, $H_{\text{hf}}^{\text{max}}$, undergo a steep drop in going from ML0 to ML4, while their variation is much weaker on further increasing the Al content beyond 6 mole %. The difference between these two field values remains approximately constant with x , indicating that the asymmetric line broadening is not primarily due to the Al substitution. This suggestion is consistent with the very weak effect of the Al upon the width σ of the MHFD. The rather broad and asymmetric distribution in field at 6 K is most likely an effect related to the non-uniform small dimensions of the maghemite particles.

Table 1. Hyperfine parameters at 6 K obtained from the fits with one distribution of hyperfine fields. $H_{\text{hf}}^{\text{max}}$ and \bar{H}_{hf} are the maximum probability and average hyperfine fields; σ is the half-width of the distribution, Γ is the FWHM and δ the isomer shift. The fields ranged from 400 kOe up to 540 kOe at steps of 5 kOe.

Sample	$H_{\text{hf}}^{\text{max}}$ (kOe)	\bar{H}_{hf} (kOe)	σ (kOe)	Γ (mm/s)	δ (mm/s)
ML0	523	506	24	0.43	0.47
ML4	512	498	25	0.45	0.47
ML6	509	495	26	0.46	0.47
ML14	510	495	27	0.46	0.47
ML18	509	492	28	0.45	0.47

The magnetically split spectra at temperatures of 80 K and beyond have been analysed in the same manner as the 6 K ones, with a field range of 70–550 kOe and step of 10 kOe. Where an additional doublet is present, a superimposed quadrupole-splitting distribution (QSD) was included. The quadrupole splitting, ΔE_{Q} , was allowed to vary between 0.0 and 2.5 mm/s in steps of 0.1 mm/s. Line width and fractional area were adjusted, as well as a linear correlation between δ (center shift) and ΔE_{Q} . Figure 2 shows that, as far as reproducing the experimental data is concerned, the MHFD adequately describes the observed spectra. Some relevant doublet and sextet parameters for ML0 at selected temperatures are listed in Table 2.

The maximum of $p(H_{\text{hf}})$ in the vicinity of $H_{\text{hf}} = 100$ kOe (Figure 2) is believed to be unreal and most likely due to an artifact of the fitting procedure. Le Caer *et al* (1984) has demonstrated that in situations where large quadrupole splittings (see below) coexist with a very broad MHFD, the model used to extract the $p(H_{\text{hf}})$ values is not correct for the lower hyperfine fields and results in large errors on the line positions and intensities. As a consequence of this spurious maximum, the average hyperfine field, \bar{H}_{hf} , as calculated in the fitting program, has no physical meaning.

The $H_{\text{hf}}^{\text{max}}$ data in Table 2 refer to the high-field maximum of the $p(H_{\text{hf}})$ histograms. For temperatures above 300 K this maximum field is rather poorly defined, due to the extreme broadening of the lines, and consequently its temperature dependence could not be properly estimated. In contrast, it has been recently shown that the Brillouin function accounts reasonably well for the $H_{\text{hf}}(T)$ behavior of relatively well-crystallized Al-maghemites (da Costa *et al* 1994b). Of course, one has to bear in mind that temperature-dependent phenomena which affect the hyperfine field, such as collective magnetic excitations (Mørup and Topsøe 1976) and surface-induced field reductions (Van der Kraan 1973), are not included in the simple molecular field approximation. These effects are substantial for the poorly crystalline ML samples, but much less so for the better crystallized M samples.

At temperatures exceeding approximately 160 K the

Table 2. Hyperfine parameters for sample ML0 at some selected temperatures. Isomer shifts are related to \overline{H}_{hf} and $\overline{\Delta E}_{\text{Q}}$. QSD calculated from 0 to 2.5 mm/s (step = 0.1 mm/s) and MHFD from 70 to 550 kOe for the sextet (step = 10 kOe). At 100 K and 475 K the sextet line width (Γ) was fixed at 0.35 mm/s; σ is the half-width of the distribution and RA is the relative area.

T (K)	SEXTET						DOUBLET					
	$H_{\text{hf}}^{\text{is}}$ (kOe)	\overline{H}_{hf} (kOe)	σ (kOe)	Γ (mm/s)	δ (mm/s)	RA (%)	$\overline{\Delta E}_{\text{Q}}$ (mm/s)	$\Delta E_{\text{Q}}^{\text{is}}$ (mm/s)	δ (mm/s)	σ (mm/s)	Γ (mm/s)	RA (%)
475	346	266	117	0.35	0.26	46	0.78	0.66	0.25	0.37	0.40	54
300	403	288	124	0.35	0.34	59	0.77	0.66	0.33	0.36	0.38	41
100	491	422	109	0.49	0.42	98	0.66	*	0.36	0.43	0.31	2
80	498	445	94	0.46	0.43	100	—	—	—	—	—	—

* The maximum of the distribution is so ill defined that no reasonable value can be assigned to it.

spectra of the Al-substituted samples only consist of a slightly asymmetric doublet due to the superposition of the A- and B-site contributions. Two quadrupole doublets with split-Lorentzian line shape (i.e., different width for the low- and high- ΔE_{Q} side of the absorption line) were considered to fit the MS, however, with two rather severe constraints: the A-site isomer shifts were forced to be $\delta_{\text{A}} = \delta_{\text{B}} - 0.08$ mm/s, and the relative area ratios were fixed at their values found from external-field measurements (da Costa *et al* 1994a). The idea behind the isomer-shift coupling is that the difference $\delta_{\text{B}} - \delta_{\text{A}}$ for the M samples was found to be constant at 0.12 mm/s over a wide range of temperatures (da Costa *et al* 1994c). The presently used value of 0.08 is the average of ten external-field results, all at 4.2 K and referring to poorly crystalline maghemites (de Bakker *et al* 1991, da Costa *et al* 1994a). Presently it is not yet established whether the lower value of the isomer-shift difference for nano-sized maghemite is an intrinsic property or merely an artifact resulting from the strong overlap of the A- and B-site components in the external-field MS. Nevertheless, utilizing the constraint $\delta_{\text{B}} - \delta_{\text{A}} = 0.12$ was found to produce insignificant changes for the remaining Mössbauer parameters. The agreement between the experimental and fitted doublet spectra is satisfactory (Figure 2), and within the errors, the derived A- and B-site quadrupole splittings were found to be temperature independent. The average values, calculated from all data between 220 and 475 K, are given in Table 3.

Despite the fact that the local structural symmetry

Table 3. A- and B-site quadrupole splittings ($\Delta E_{\text{Q,A}}$ and $\Delta E_{\text{Q,B}}$ respectively) obtained from the spectra taken from 220 K up to 475 K. $T_{1/2}$ and T_0 were calculated from the relative area of the doublet fraction.

Sample	T_0 (K)	$T_{1/2}$ (K)	$\Delta E_{\text{Q,A}}$ (mm/s)	$\Delta E_{\text{Q,B}}$ (mm/s)
ML0	92	390	—	—
ML4	79	146	0.86 ± 0.04	0.65 ± 0.01
ML6	64	118	0.85 ± 0.02	0.64 ± 0.01
ML14	68	118	0.91 ± 0.02	0.66 ± 0.01
ML18	48	100	0.93 ± 0.05	0.68 ± 0.03

of the tetrahedra is essentially cubic, the A-site quadrupole splitting is found to be larger than that for the B sites. This is, however, not uncommon and several other ferric spinel oxides display the same behavior (Vandenberghe and De Grave 1989). The reason for this is that the symmetry of the charge distribution around the central A-site iron deviates from cubic. In the case of maghemite, this deviation is due to the vacancies in the surrounding B sites. According to the data in Table 3 there seems to exist a weak positive correlation between the A- and B-site quadrupole splittings and the Al content. However, taking into account the uncertainties, one must conclude that it is not feasible to estimate the mole % Al in an unknown maghemite sample on the basis of the fitted quadrupole splittings.

Figure 3 shows the relative doublet area of samples ML0, ML4, ML14, and ML18 as a function of temperature. The variation for ML6 nearly coincides with that for ML14, and is, therefore, not included in the drawing. Two different characteristic temperatures have been derived from the data shown in Figure 3:

- $T_{1/2}$, which is the temperature corresponding to a 50/50 doublet-sextet spectrum
- T_0 , the temperature below which the doublet ceases to exist.

Both $T_{1/2}$ and T_0 (see Table 3) show a steady decrease with increasing Al content. Again, it is not straightforward whether this decrease is solely due to the Al, or whether a decreasing of the particle size plays a role as well. In this respect it is to be recalled that it was not possible to accurately calculate the particle sizes due to the huge line-broadening in the XRD patterns.

The doublet component in a mixed spectrum of maghemite at a given temperature is associated with those particles which undergo superparamagnetic relaxation at that temperature. It was indeed observed in the present study, as well as in an earlier study by Hendriksen *et al* (1993), that a doublet was no longer apparent in the spectrum recorded in the mixed temperature region and with the absorber subjected to a strong applied field. Surprisingly, the doublet fraction

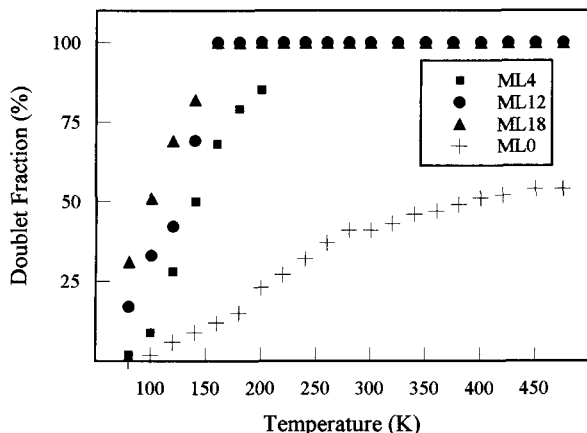


Figure 3. Variation of the fractional doublet area with temperature for samples with different Al contents.

for sample ML0 increases drastically slower with increasing T as compared to the Al-substituted samples. It has been claimed in the literature that the existence of an extremely broad temperature range for mixed sextet/doublet MS is indicative for the absence of magnetic interactions between the superparamagnetic particles (Koch *et al* 1986, Prené *et al* 1993). If this were true, then the question arises why such inter-particle interactions are strong in the case of the aluminous maghemites, while non-existing in the Al-free sample. This is undoubtedly an intriguing observation which deserves further attention.

The temperature variations $\delta(T)$ of the average isomer shifts are very much alike for the five investigated samples. An example is shown in Figure 4 and refers to ML14. It is well known that experimental $\delta(T)$ curves

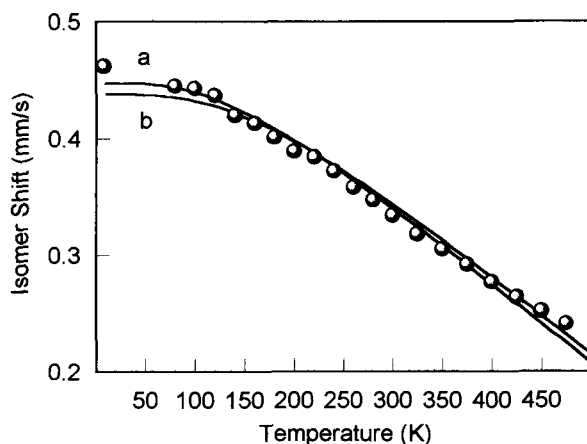


Figure 4. Temperature dependence of the average isomer shift of sample ML14. Solid lines are the calculated behavior as predicted by the Debye model with $\theta_M = 520$ K and $\delta_I = 0.588$ mm/s (a); dotted line refers to $\theta_M = 610$ K and $\delta_I = 0.603$ mm/s (b).

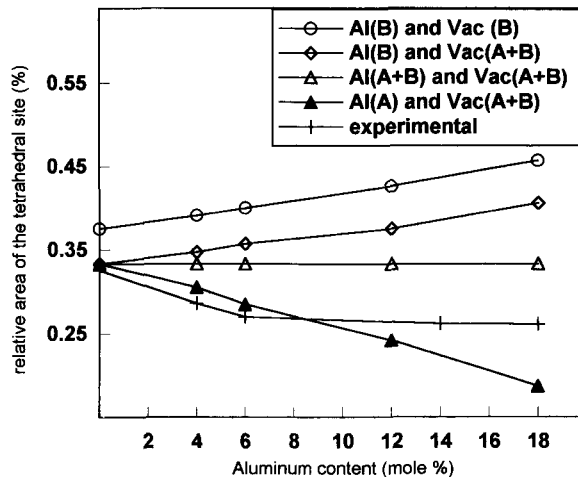


Figure 5. Theoretical and experimental tetrahedral area-ratio as a function of the Al content. The experimental data were obtained from the measurements at 4.2 K in an external field of 60 kOe. Solid lines are a guide for the eye.

in general are very well reproduced by a simple model based upon the Debye approximation of the lattice vibrations. That model contains a quantity, called the *characteristic Mössbauer temperature* (θ_M), the value of which can be determined from the observed data. A second parameter appearing in the model is the so-called *intrinsic isomer shift* (δ_I), which to a good approximation is temperature-independent. To some extent, the magnitude of θ_M is related to the strength of the chemical Fe-O bond. However, as pointed out by De Grave and Van Alboom (1991), numerous and highly precise isomer-shift data are required in order to retrieve reliable information in that respect. Such data are not available for the currently studied maghemites, and therefore, it was not attempted to fit the observed $\delta(T)$ variations. The full curves a and b plotted in Figure 4 were calculated from the model assuming $\theta_M = 530$ K, $\delta_I = 0.588$ mm/s and $\theta_M = 610$ K, $\delta_I = 0.603$ mm/s respectively. These θ_M values are typical for Fe^{3+} in a variety of compounds, including spinel ferrites (De Grave and Van Alboom 1991) and well crystallized maghemites (da Costa *et al* 1994b). The two curves match the experimental data points reasonably well.

The external-field MS for the aluminous maghemites prepared from hematites and sucrose (the M samples, for which $\text{MCD} \sim 35$ nm) showed that the B-site hyperfine field did not change with Al substitution, whereas for the A site a gradual decrease was observed. This fact, together with the observed A- to B- site area ratio of close to 40:60 for all samples, was explained by assuming that the Al ions are located in the octahedral sites (Bowen *et al* 1994). This seems not to be the case for the samples used in the present study. The fractional area of the A-site absorption, determined from

the applied-field MS, is plotted as a function of Al substitution in Figure 5, together with values expected on the basis of some specific assumptions. The trend shown by the experimental data seems to rule out the possibility that all Al is on octahedral sites with vacancies either on B sites or distributed at random among A and B sites. The two other situations which are considered in Figure 5, i.e., both Al ions and vacancies at random on A and B sites, or all Al on A sites and vacancies at random on A and B, better match the observed correlation. A more precise determination of the Al and vacancy distribution remains not feasible, and much stronger fields are required to fully resolve the strongly overlapping sextet components.

The method used to synthesize aluminous maghemites apparently plays an important role in determining the structural characteristics of the final products. Also the amount of Al that can substitute for Fe seems to depend on the way of synthesis. Gillot and Rousset (1990) found that up to 66 mole % of Al can be incorporated in maghemite prepared from an organic precursor, whereas Wolska and Schwertmann (1989) proposed a limit of 10 mole % for samples prepared from inorganic precursors. The present results for \bar{H}_{hf} (6 K), $T_{1/2}$, T_0 , $\Delta E_{Q,A}$ and $\Delta E_{Q,B}$ seem not to confirm the existence of such low limit, but the reliability of these quantities must be examined prior to any claiming in that respect. Firstly, it is the authors' experience that the average hyperfine field as derived from MHFD is influenced by the field range used to adjust the spectra. Although the same field range was used for all samples, it is probable that the distribution of hyperfine fields for different samples are not the same. On the contrary, the maximum-probability field is little affected by the chosen field range. Secondly, the errors in the A- and B-site quadrupole splittings are relatively large (Table 3), making these two quantities not quite suitable for the purpose of checking for the existence of a substitution limit. Finally, $T_{1/2}$ and T_0 were derived from the relative areas of the doublet component, and these too are affected with a large error due to the extremely broad lines for the sextet component, which overlaps significantly with the superparamagnetic doublet. On the other hand, both the maximum-probability fields at 6 K (Table 1) and the A- and B-site hyperfine-field values obtained from the external-field MS (da Costa *et al* 1994a) do suggest a substitution limit of approximately 10 mole % in the present maghemites. These two last parameters are beyond any doubt the most reliable ones because the A- and B-site components are clearly separated in these external-field spectra. In conclusion, it is clear from the present results that a final and firm decision about the existence of a substitution limit will only be possible if spectra in much stronger external fields will become available. Such experiments in a field of 15 T are planned for the near future.

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