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^{57}Fe MÖSSBAUER EFFECT STUDY OF Al-SUBSTITUTED LEPIDOCROCITES†

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Abstract—Seven Al-containing lepidocrocite samples, γ-$Fe_{1-x}Al_xOOH$, prepared from $FeCl_2/Al(NO_3)_3$ solutions with initial Al/(Al + Fe) mole ratios C_i of 0.0025, 0.01, 0.025, 0.05, 0.075, 0.10 and 0.15 mol/mol, were examined by means of Mössbauer spectroscopy at room temperature (RT) and at various temperatures in the range of 8 to 80 K. The spectra at RT and 80°K consist of broadened quadrupole doublets and were analyzed in terms of a single doublet and of a model-independent quadrupole-splitting distribution, the latter yielding the best fit. The observed variations of the quadrupole-splitting parameters with increasing C_i are inconclusive as to whether the Al cations are substituting into the structure. The temperature at which the onset of magnetic ordering is reflected in the spectra, was measured by the thermoscan method with zero source velocity. A gradual shift from 50 K for C_i = 0.0025 mol/mol to 44 K for C_i = 0.10 mol/mol was observed for that temperature. As compared to earlier studies of Al-free γ-FeOOH samples with similar morphological characteristics, the fractional doublet area in the mixed sextet-doublet spectra at 35 K is significantly higher for the present lepidocrocites. This observation is ascribed to the substitution of Al cations into the lepidocrocite structure. A similar conclusion is inferred from the variation with C_i of the maximum-probability hyperfine field derived from the spectra recorded at 8 K and fitted with a model-independent hyperfine-field distribution. The magnetic results suggest that for the sample corresponding to C_i = 0.15 mol/mol, not all of the initially present Al has been incorporated into the structure.

Key Words—Al Substitution, Lepidocrocite, Mössbauer Spectra.

INTRODUCTION

Some years ago, Schwertmann and Wolska (1990) concluded from precise X-ray diffraction (XRD) analyses that lepidocrocite, γ-FeOOH, can incorporate Al into its structure, at least up to Al/(Al + Fe) concentrations of 0.1 mol/mol. The presence of Al cations was observed resulting in small, downward shifts in the unit-cell edge lengths and volume of the host lepidocrocite. It was believed that Mössbauer spectroscopy of the Al-containing samples should be a useful technique to confirm that conclusion. To the best of our knowledge, a systematic Mössbauer study of the effect of Al upon the relevant hyperfine parameters of γ-FeOOH, has not been reported. Since Al^{3+} is diamagnetic, it is to be expected that the magnetic properties, in particular the magnitude of the magnetic hyperfine field, are affected by the substitution, as they are in other, more common iron oxides and oxyhydroxides (Bowen et al. 1993). In this paper, the authors report the results of such a Mössbauer study. In many instances, these results will be compared to those obtained earlier by De Grave et al. (1986) for non-substituted lepidocrocites (samples P23, L86, L121 and L147) which exhibit similar morphological characteristics, and to those presented by Murad and Schwertmann (1984) for non-substituted samples, P23 and 22/568. The latter one has a considerably higher degree of crystallization.

EXPERIMENTAL

Samples used were prepared by oxidation of $FeCl_2/Al(NO_3)_3$ solutions with Al-to-(Al + Fe) fractions C_i of 0.0025, 0.01, 0.025, 0.05, 0.075, 0.10 and 0.15 mol/mol, and characterized by Schwertmann and Wolska (1990). The Al/(Al + Fe) ratios, x, in the final solid products, designated as γ-$Fe_{1-x}Al_xOOH$, were determined analytically from the above prepared samples as 0.0047, 0.0141, 0.0265, 0.0598, 0.0785, 0.1031 and 0.141 respectively, and are somewhat different from the initial solution compositions, especially for the lower ones. The samples are code-named LS02, LS1, LS2, LS5, LS7, LS10 and LS15. The particle size, quantified by the mean coherence length along the b-axis, MCL_b, was found to decrease from ≈27 nm for LS02 to ≈3 nm for LS15. A similar particle size range of 19-to-3.5 nm was estimated for the Al-free P and L samples. Sample 22/568 has MCL_b = 66 nm (Murad and Schwertmann 1984).

Mössbauer spectra (MS) at room temperature (RT)

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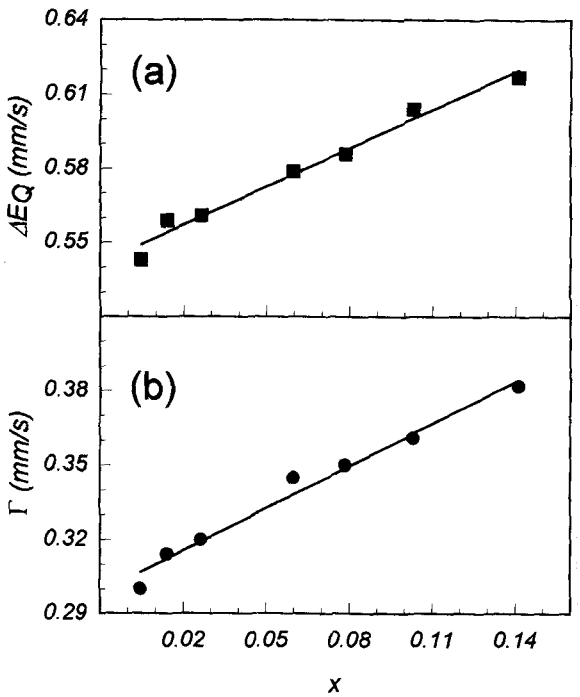


Figure 1. Quadrupole splitting ΔE_Q (a) and line width Γ (b) for the lepidocrocite samples at room temperature plotted as a function of the Al content x in γ-$Fe_{1-x}Al_xOOH$. The Mössbauer spectra were fitted with a symmetrical quadrupole doublet. The solid lines are the linear-regression lines.

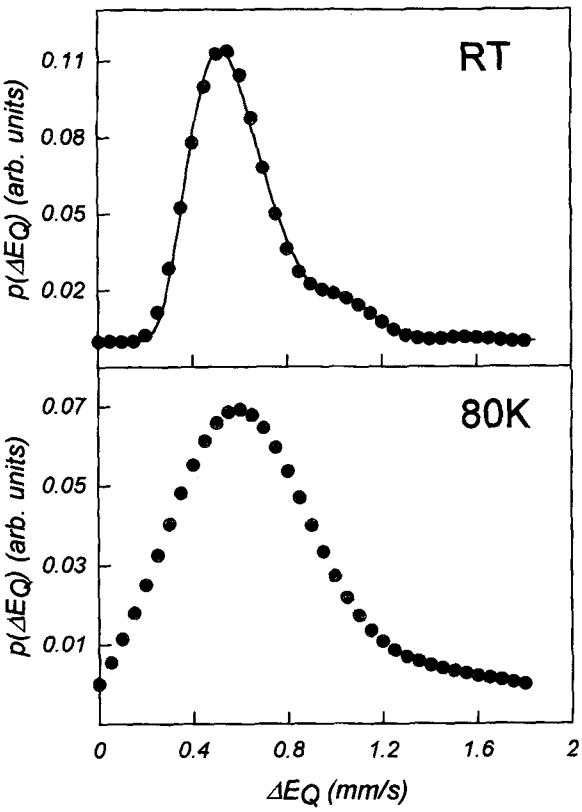


Figure 2. Quadrupole-splitting distribution profiles $p(\Delta E_Q)$ of the LS07 Al-lepidocrocite at room temperature and 80 K. The size of the symbols corresponds to the step (0.05 mm/s) at which the quadrupole splitting was allowed to vary within the range 0.0–1.8 mm/s. The full line in (RT) represents the superposition of two log-normal distributions adjusted to the calculated probability values.

and at variable temperatures in the range $T \leq 80$ K were obtained with a time-mode spectrometer operating in the constant-acceleration mode. The data were collected on 1024 channels. Velocity calibration was carried out either interferometrically or by using the MS of standard absorbers. Doublet MS were recorded in the velocity range ±4 mm/s and magnetically split ones in ±12 mm/s. All center-shift values quoted hereafter are with respect to α-Fe at RT. The instrumental width of the spectrometer was approximately 0.22 mm/s. The temperatures T_B referring to the transition from a pure doublet spectrum to a spectrum in which the onset of magnetic ordering is reflected, were determined by the so-called thermo-scan method. This method measures the γ-transmission as a function of T with the source having zero velocity (Chambaere and De Grave 1984).

RESULTS AND DISCUSSION

All MS at RT and 80 K are doublets. There is no indication whatsoever that a goethite-phase impurity would be present in any of the lepidocrocites. When fitted with symmetrical, Lorentzian-shaped quadrupole doublets, the obtained quadrupole splittings ΔE_Q and line widths Γ are observed to increase with increasing x. Figure 1 depicts the RT data in that respect. The correlations derived from the 80 K spectra show the same trends, are less smooth and the data for LS15 are not similar to those for the lower concentrations. For samples 22/568 and P23, Murad and Schwertmann (1984) found for ΔE_Q at RT, the value of 0.527 and 0.550 mm/s and for Γ at RT, the value of 0.256 and 0.311 mm/s. The variations obtained for these two quantities (see Figure 1) are clearly more pronounced, especially in the case of ΔE_Q. This could point to an effect associated with an Al-for-Fe substitution. However, it is believed that the observed behavior of the two quantities is not firmly conclusive in that respect.

The goodness-of-fit improved significantly that is χ^2 decreased, if a model-independent quadrupole-splitting distribution was used to describe the MS rather than a single doublet. Example distribution profiles, $p(\Delta E_Q)$, referring to sample LS7 at RT and 80 K, are reproduced in Figure 2. The range for ΔE_Q was 0.0 to 1.8 mm/s at steps of 0.05 mm/s. The values for the order of smoothing (3) and the smoothing parameter γ (0.001) (Wivel and Mørup 1981; Amarasiriwardena et al. 1986; Vandenberghe et al. 1994) were chosen, after several trial fits of a few selected MS. All probability

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Table 1. Positions $\Delta E_{Q,1}^{m}$, $\Delta E_{Q,2}^{m}$, widths σ_1, σ_2, and relative area S_1 of the most dominant component of the two log-normal distributions fitted to the quasi-continuous quadrupole-splitting distributions derived from the room-temperature Mössbauer spectra of the Al lepidocrocites prepared from $FeCl_2/Al(NO_3)_3$ solutions with various Al/(Al+Fe) fractions C_i.

C_i (mol/mol)	$\Delta E_{Q,2}^{m}$ (mm/s)	σ_1 (mm/s)	$\Delta E_{Q,1}^{m}$ (mm/s)	σ_2 (mm/s)	S_1
0.0025	0.50	0.25	1.03	0.07	0.97
0.010	0.51	0.28	1.05	0.10	0.95
0.025	0.51	0.28	1.04	0.09	0.95
0.050	0.51	0.31	1.06	0.11	0.96
0.075	0.51	0.30	1.07	0.10	0.95
0.10	0.53	0.32	1.09	0.10	0.95
0.15	0.53	0.36	1.08	0.08	0.98

values p were forced to be positive or zero, a condition that is imposed by a nonlinear programming procedure (Le Caër and Dubois 1979). Finally, in order to account for the slight asymmetry in peak depths, an adjustable linear correlation between δ and ΔE_Q was included in the fitting procedure. Its iterated slope was always small, typically an order of 0.01, and not related to any other parameter.

Similar to the results obtained earlier for the non-substituted lepidocrocites (De Grave et al. 1986), the $p(\Delta E_Q)$ profiles derived from the RT spectra of the present LS samples also suggest the presence of two more or less distinct components, one with quadrupole splittings centered around ≈0.5 mm/s and the second, less abundant one with quadrupole splittings centered around ≈1 mm/s. Again, two log-normal distributions, each one characterized by a maximum-probability value ΔE_Q^m and a width σ, were adjusted to the $p(\Delta E_Q)$ profiles. The numerical data are listed in Table 1. The variations observed for the two $\Delta E_{Q,i}^m$ and σ_i values (i = 1, 2) almost exactly coincide with those reported to occur for the pure lepidocrocites by De Grave et al. (1986), and can be attributed exclusively to the variation in particle size. [It is noted that a typographical error in expression (2) (De Grave et al. 1986) has remained unnoticed. This expression, relating the maximum-probability splitting to the mean value μ, should read: $\Delta E_Q^m = \mu \exp(-\sigma^2)$.] As for the distribution profiles resolved from the 80 K spectra, the shoulder in the vicinity near ΔE_Q = 1 mm/s is much less pronounced and for LS7 (Figure 2) and higher, the iteration routine for adjusting a superposition of two log-normals failed to reach proper convergency. For the aforementioned Al-free L147 lepidocrocite, the widths σ_1 of both adjusted log-normal distributions were found to increase gradually with decreasing temperature (De Grave et al. 1986). This implies a stronger overlap of the two closely spaced ΔE_Q distributions, one of which constitutes only 5% of the total absorption, which explains the featureless distribution profiles at 80 K, unlike those derived from the RT spectra.

The high-ΔE_Q satellite component resolved from the calculated $p(\Delta E_Q)$ profiles was tentatively ascribed by De Grave et al. (1986) to iron species near the surface of the non-substituted lepidocrocite particles, a suggestion which emerged from the observation of a clear negative correlation between the specific surface area, and the area contribution of the satellite component to the total profile. Due to strong deformations of their coordinations, these surface irons are indeed expected to exhibit larger quadrupole splittings as compared to species located inside the particle. For the Al-containing samples, the variation of the fractional areas of the two log-normal components (S_1 values listed in Table 1) with the particle size is considerably less pronounced. This finding makes the earlier interpretation concerning the origin of the high-ΔE_Q component less convincing, unless the surface coordinations were preferentially occupied by Al cations. However, this cannot be concluded firmly from the present experiments. The observed lack of variations of the area parameter S_1 further implies that the high quadrupole splittings are generally not related to the peculiar morphology of the lepidocrocite plates as visualized from the electron micrographs. For low Al contents, including x = 0.0, these plates exhibit strongly serrated edges. This typical morphology, however, becomes less expressed with increasing Al content (Schwertmann and Wolska 1990) and for $x \geq 0.05$ the edges are rounded-off.

Also at low temperatures (T < 50 K) the MS of the LS samples are all very similar to those observed for the Al-free samples. In a relatively broad temperature interval, they consist of a superposition of an asymmetrically broadened sextet and a quadrupole doublet, the contribution of the latter decreasing with decreasing temperature. The transition from a pure doublet spectrum to a pure sextet spectrum as the temperature lowers, proceeds in a similar manner for all six investigated products. The transition curves for samples LS02 to LS10 are reproduced in Figure 3. The onset of magnetic ordering occurs at ≈50 K for LS02, which is considerably lower than in the case of the well-crystallized 22/568 lepidocrocite, namely 77 K (Murad and Schwertmann 1984), but comparable to the results for the non-substituted samples with poor crystallinity (De Grave et al. 1986). The dashed line in Figure 3 shows that there appears to be a gradual, downward shift of the transition range by about 5 K from LS2 to LS10. This variation can be understood if it can be presumed that the Al cations are incorporated into the γ-FeOOH structure. A more convincing argument in support of this latter suggestion was found from the value of the fractional area A_D of the doublet component at T = 35 K at which all samples exhibit mixed doublet and sextet spectra. This fractional area is plotted against x in Figure 4 and is observed to increase monotonically up to LS10. A levelling-off at a value

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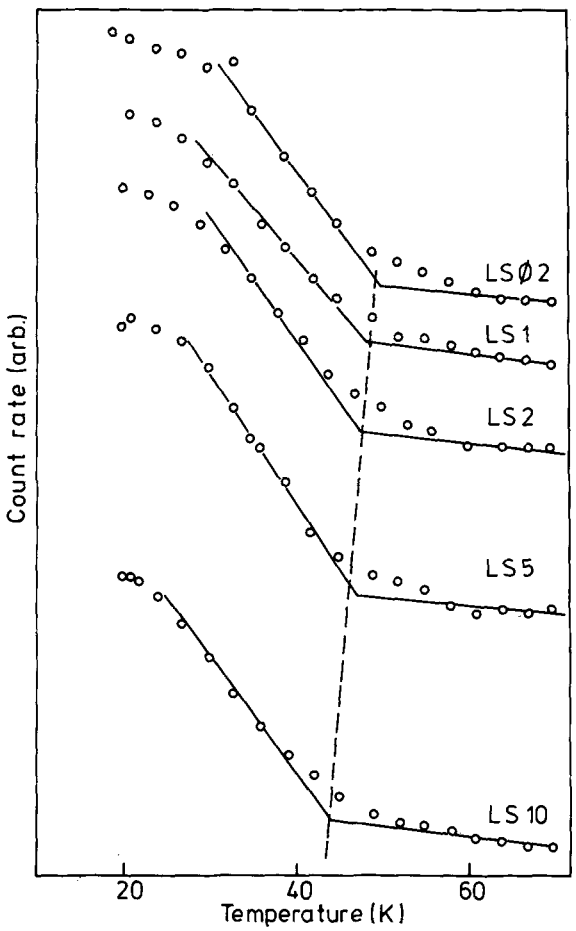


Figure 3. Thermo-scan curves measured for 5 of the 7 investigated lepidocrocite samples. The dashed line shows the slight decrease with increasing initial Al contents C_i of the temperature at which the onset of magnetic ordering is detected.

of $A_D = 0.48 \pm 0.05$ seems to occur beyond that concentration. For the Al-free lepidocrocites, A_D at 35 K ranges between 0.0 and 0.13 (De Grave et al. 1986) and is not related to MCL_b. The significantly lower values as compared to the results obtained for the present samples, are in the authors' opinion a strong indication that the Al species are incorporated in the structure of these latter lepidocrocites, at least for Al/(Al + Fe) ratios of up to 0.10 mol/mol in the initial solution. This finding supports the observed diminution of the unit cell (Schwertmann and Wolska 1990).

The MS at 8 K of all LS samples consist of an asymmetrically broadened Zeeman pattern, characteristic for a broad hyperfine-field (H_{hf}) distribution. Example spectra, referring to samples LS1 and LS10, are reproduced in Figure 5, clearly showing the effect of an increased Al content and/or an increased specific surface area on the line broadening. The distribution in fields is believed to be due primarily to Al-for-Fe

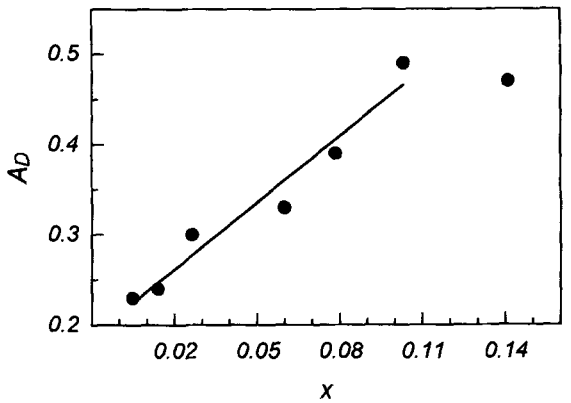


Figure 4. Fractional doublet area A_D in the mixed Mössbauer spectra recorded at 35 K plotted as a function of the Al content x. Solid curve serves as a guide for the eye.

substitution and/or surface effects, since other mechanisms suggested to produce field distributions, such as collective magnetic excitations (Mørup and Topsøe 1976), cluster magnetic ordering (Bocquet et al. 1992) or superferromagnetism resulting from inter-particle magnetic interactions (Mørup and Tronc 1994) have but a minor effect at that low temperature. The 8 K spectra were fitted with a model-independent H_{hf} dis-

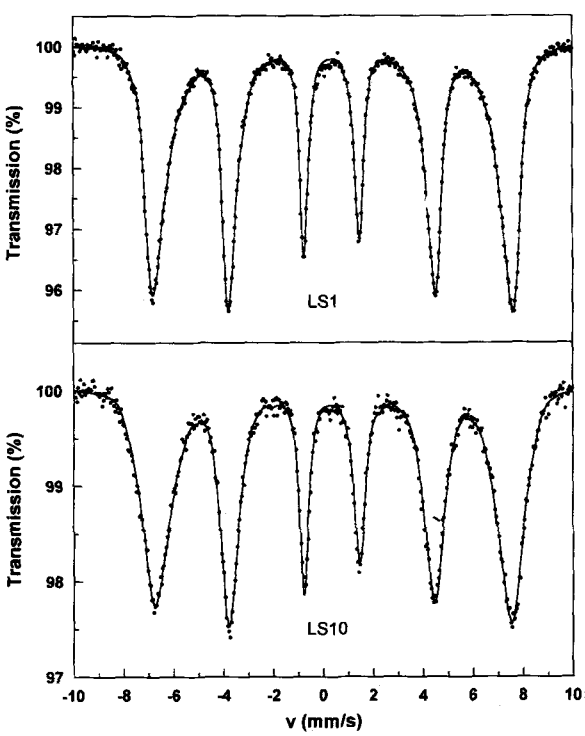


Figure 5. Mössbauer spectra at 8 K of the Al-lepidocrocite samples LS1 and LS10. The full curves are the adjusted spectra calculated with a model-independent distribution of hyperfine fields.

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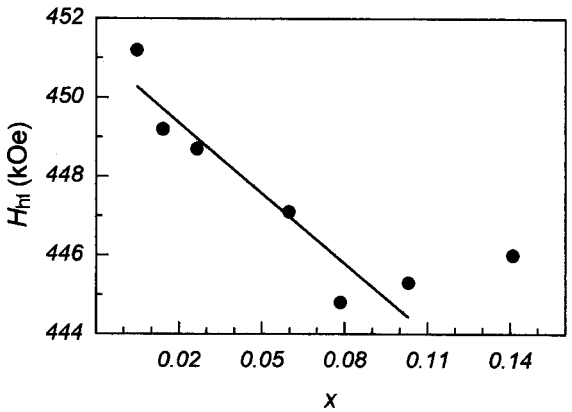


Figure 6. Maximum-probability hyperfine field H_{hf}^{m} derived from the 8 K Mössbauer spectra plotted as a function of the Al content x. Solid curve is the linear-regression line for data of samples LS02 to LS10.

tribution. We observed that the adjusted values for the maximum-probability field, H_{hf}^{m}, and especially for the average hyperfine field, depended upon the conditional parameters specified for the hyperfine-field distribution. Excellent fits were obtained for fields covering the range 225–525 kOe at steps of 5 kOe, third-order smoothing and smoothing parameter $\gamma = 0.0001$. Linear correlations between the hyperfine field, and the quadrupole and center shifts, were also taken into account. Although they improved the goodness-of-fit to a significant level, no physical meaning could be attributed to the adjusted correlation coefficients.

The H_{hf}^{m} values obtained under the above specified conditions are plotted as a function of the concentration parameter x in Figure 6. Excluding the result for sample LS15, the variation with x can be approximated by the following linear expression:

$$H_{hf}^{m} = 450.6 - 59.5x \qquad (r = -0.95 \text{ for } n = 6) \qquad [1]$$

For all respective samples, the deviation between the numerically adjusted H_{hf}^{m} value and the value calculated from Equation [1] is not more than 1 kOe. This is considered to be within the experimental error limits. This was not the case if the value obtained for LS15 was included in the linear regression.

Several trial fits using different field ranges and/or different smoothing conditions imposed on the distribution profiles, have shown that the intercept H_{hf}^{m} (0) on the ordinate axis and the slope of the linear-regression line do not vary by more than 3 and 5 kOe, respectively. For the aforementioned non-substituted lepidocrocites, the adjusted maximum-probability fields at T = 13 K are scattered within the range 444 ± 2 kOe. These somewhat lower values as compared to H_{hf}^{m} (0) are explained by the fact that this latter value refers to a temperature which is closer to saturation. Hence, the presently observed variation of H_{hf}^{m} with Al by 6 kOe cannot be ascribed exclusively to particle-size effects, and a significant contribution must result from the Al-for-Fe substitution within the lepidocrocites' structure.

The field reduction in γ-FeOOH resulting from the presence of Al cations within its structure and as quantified by the slope appearing in Equation [1], is comparatively high. For α-FeOOH (Murad and Schwertmann 1983), α-Fe_2O_3 (De Grave et al. 1982) and γ-Fe_2O_3 (Bowen et al. 1994), the authors report reductions in the range 30 to 40 kOe per unit Al/(Al + Fe) and at temperatures close to saturation. Therefore, it is conceivable that the presently observed linear variation contains a contribution from the decreasing crystallinity. Murad and Schwertmann (1983) correlated the hyperfine field at 4.2 K, obtained by fitting a single Lorentzian-shaped sextet to the MS, of Al goethites to both the Al concentration, x, and the surface area, S, expressed in m^2/g:

$$H_{hf} = 505.4 - 33x - 0.036S \qquad (r = -0.98, \text{ for } n = 19) \qquad [2]$$

On the basis of the measured MCL_b values and the experimental data for MCL_b and S from the earlier studied non-substituted γ-FeOOH samples, the surface area for the present samples LS02 to LS10 is estimated to vary within the range ≈60–120 m^2/g. If, for the sake of simplicity, it is assumed that a H_{hf}^{m} – S correlation similar in magnitude to that appearing in the multiple regression (Equation [2]) for goethite is valid for lepidocrocite as well, then the H_{hf}^{m} – x regression factor would be approximately −40 kOe per unit of x. This seems to be a reasonable value for the Al-induced hyperfine-field reduction.

In summary, both the variation of the fractional doublet area at 35 K and that of the low-temperature, maximum-probability hyperfine field indicate that Al is present at the Fe sites in the investigated samples. This finding supports the concluded Al-for-Fe substitution on the basis of the observed reduction in the unit-cell parameters (Schwertmann and Wolska 1990). However, Figures 4 and 6 suggest that for the LS15 sample, as compared to LS10, no additional Al was incorporated into the lepidocrocite structure. This is also consistent with the measured value of the c edge length of that sample, which is larger than for the samples obtained from initial solutions with $C_i \geq 0.05$. The observed effects that the Al exerts on the magnetic properties are all explained by the non-magnetic nature of the Al^{3+} cations. It has been argued for poorly crystalline, non-substituted γ-FeOOH that the mixed sextet-doublet spectra at temperatures in the magnetic order-disorder transition range reflect the simultaneous presence of paramagnetic, rather than superparamagnetic, grains and magnetically ordered grains, and hence that the Néel temperature T_N exhibits

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a distribution. The arguments in that respect were based on external-field MS at 55 K (De Grave et al. 1986). On increasing the Al content, the overall magnetic interactions weaken, and T_N shifts to lower values. According to the simple molecular-field approach for the magnetic ordering in a two-sublattice antiferromagnet, T_N for a given crystallite can be written as $T_N(x) = T_N(0)\ (1 - x)$, with x representing the concentration of non-magnetic species in the crystallite (De Grave et al. 1982). The maximum $T_N(0)$ value for the present lepidocrocites is around 50 K, so that a substitution degree of $x = 0.10$ implies a downward shift of 5 K, which agrees well with the observations reproduced in Figure 3. The distribution of Néel temperatures and the lowering of their values, further explain the increase of the doublet fraction A_D at a given temperature with increasing Al content. Finally, the negative correlation between the most abundant saturation hyperfine field and the Al content, can be understood on the basis of the well-known supertransfer mechanism. With increasing Al, the number of Al-O-Fe paths increases so that on the average the supertransfer of 3d-spin density into the outer s shell of the probe iron nuclei, and hence the total hyperfine field, decreases.

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REFERENCES

Amarasiriwardena DD, De Grave E, Bowen LH, Weed SB. 1986. Quantitative determination of aluminum-substituted goethite-hematite mixtures by Mössbauer spectroscopy. Clays & Clay Miner 34:250–256.

Bocquet S, Pollard RJ, Cashion JD. 1992. Dynamic magnetic phenomena in fine-particle goethite. Phys Rev B 46:11657–11664.

Bowen LH, De Grave E, Vandenberghe RE. 1993. Mössbauer effect studies of magnetic soils and sediments. In: Long GJ, Grandjean F, editors. Mössbauer spectroscopy applied to magnetism and materials science. Vol. 1. New York:Plenum Press. 115–159.

Bowen LH, De Grave E, Bryan AM. 1994. Mössbauer studies in external field of well-crystallized Al-maghemites made from hematite. Hyperfine Interact 94:1977–1982.

Chambaere D, De Grave E. 1984. On the Néel temperature of β-FeOOH: structural dependence and its implications. J Magn Magn Mater 42:263–268.

De Grave E, Bowen LH, Weed SB. 1982. Mössbauer study of aluminum-substituted hematites. J Magn Magn Mater 27:98–108.

De Grave E, Persoons RM, Chambaere DG, Vandenberghe RE, Bowen LH. 1986. An ^{57}Fe Mössbauer effect study of poorly crystalline γ-FeOOH. Phys Chem Minerals 13:61–67.

Le Caër G, Dubois JM. 1979. Evaluation of hyperfine parameter distributions from overlapped Mössbauer spectra of amorphous alloys. J Phys E: Sci Instrum 12:1083–1090.

Mørup S, Topsøe H. 1976. Mössbauer studies of thermal excitations in magnetically ordered microcrystals. Appl Phys 11:63–66.

Mørup S, Tronc E. 1994. Superparamagnetic relaxation of weakly interacting particles. Phys Rev Lett 72:3278–3281.

Murad E, Schwertmann U. 1983. The influence of aluminium substitution and crystallinity on the Mössbauer spectra of goethite. Clay Miner 18:301–312.

Murad E, Schwertmann U. 1984. The influence of crystallinity on the Mössbauer spectrum of lepidocrocite. Mineral Mag 48:507–511.

Schwertmann U, Wolska E. 1990. The influence of aluminum on iron oxides. XV. Al-for-Fe substitution in synthetic lepidocrocite. Clays & Clay Miner 38:209–212.

Vandenberghe RE, De Grave E, de Bakker PMA. 1994. On the methodology of the analysis of Mössbauer spectra. Hyperfine Interact 83:29–49.

Wivel CO, Mørup S. 1981. Improved computational procedure for evaluation of overlapping hyperfine parameter distributions in Mössbauer spectra. J Phys E: Sci Instrum 14: 605–610.

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