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Mössbauer characterization of iron oxides and (oxy)hydroxides: the present state of the art

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Mössbauer spectroscopy is a powerful direct technique for the identification and quantification of iron oxides and (oxy)hydroxides in soils and sediments. However, further characterization with respect to structural properties such as crystallinity, Al substitution, stoichiometry, water content, etc. is rather limited. With some examples of synthetic and natural goethite and hematite sample series it is illustrated that the hyperfine parameters depend on much more structural features than the Al content and crystallinity alone. Neither the Morin transition in hematite nor the Verwey transition in magnetite is directly applicable for analytical purposes in natural samples.

1. Introduction

During the last two decades, Mössbauer spectroscopy (MS) has proved to be a very suitable tool for the characterization of iron oxides and (oxy)hydroxides in soils and sediments and its quantitative and qualitative analytical power has been extensively reviewed in a number of papers [1–7]. The main compounds involved are the (oxy)hydroxides such as goethite, ferrihydrite and lepidocrocite, and the oxides hematite, magnetite and maghemite. Because the various components commonly possess a small-particle morphology and occur mainly in close association with each other or with other minerals, the information obtained from MS is often much more direct and complementary to other experimental characterization techniques, such as X-ray diffraction and microscopy. From the continuously growing amount of information obtained from well-defined synthetic materials and the improved fitting procedures applied in the spectral analyses, one can wonder to what extent MS is able to deduce the intrinsic properties of the various components, such as particle size or crystallinity, substitution, stoichiometry, etc. In this paper some general examples will be given showing the limits of MS for analytical characterization purposes.

2. Goethite: crystallinity and aluminum substitution

As a weathering product, goethite (α-FeOOH) is the most commonly found oxyhydroxide in soils. It is usually poorly crystallized and often contains isomorphous substitutions for Fe such as Al. The Mössbauer spectrum is in most cases a doublet at room temperature (RT), whereas the spectrum at 80 K is generally magnetically splitted. Sometimes, a better crystallinity is present resulting in a magnetic spectrum at RT. Taking Mössbauer spectra at room and at liquid-nitrogen temperature is, therefore, sufficient to distinguish goethite from the other iron hydroxides and oxides.

Goethite sextets usually exhibit asymmetric lines, which broaden considerably at higher temperatures. Various effects, such as superparamagnetic relaxation [8–10], different kinds of collective magnetic excitations [11–13], inter-particle interactions (superferromagnetism) [14], cluster ordering [15] and surface effects [16] have been proposed to explain the characteristic line shapes for goethite and other small-particle systems. However, in addition to Al substitution and possible particle size distributions, it remains difficult to consider a priori the various effects involved in the complex natural samples. Therefore, applying one of those models in the spectrum analysis, which often leads to cumbersome fitting procedures, is in most cases irrelevant. Fortunately, experience has learned that the spectra can satisfactorily be described by considering a hyperfine field distribution (HFD). Model-independent distribution fitting procedures [17], which are now commonly available, are therefore sufficiently accurate for quantitative and qualitative characterization purposes. If necessary, the fitting can be improved by introducing a linear correlation between the hyperfine field and the quadrupole shift. Such kind of analysis yields two hyperfine-field values (and accordingly two quadrupole shifts in the case of a correlation), i.e., the most probable value B_{p} (and $2\varepsilon_{\mathrm{Q,p}}$) and the average value B_{av} (and $2\varepsilon_{\mathrm{Q,av}}$). The latter, however, is strongly dependent on the choice of the lower field limit in the distribution. This particularly happens in the case of overlap with doublets, which in the fitting procedure may be regarded as low-field regions of the magnetic spectrum.

The Mössbauer spectrum of goethite is directly recognized by its relatively low (most probable) hyperfine field B_{p} ($\leqslant$38.1 T at RT; $\leqslant$50.0 T at 80 K) and its quadrupole shift $2\varepsilon_{\mathrm{Q}}$ of about -0.25 mm/s, which makes MS extremely suitable as a tool for identification of this oxyhydroxide in soils and sediments. Moreover, it has been readily observed that the value of the hyperfine field, measured at a certain temperature, depends on the degree of crystallinty and aluminum substitution. From systematic studies of well-defined synthetic samples, linear equations have been proposed relating the hyperfine field to the Al content, in mole Al/(Fe + Al) and to some parameter describing the crystallinity, such as the specific surface S (in m^2/g) determined by the BET method, or the inverse mean crystallite dimension $\mathrm{MCD}(1\,1\,1)^{-1}$ (in $\mathrm{n\,m}^{-1}$) obtained from the [1 1 1] diffraction line broadening. The first linear correlation involving both crystallinity and Al substitution was suggested by Golden et al. [10] with the following equation for the hyperfine field at 77 K:

$$B(77\ \mathrm{K}) = 49.8 - 13.6\,\mathrm{Al} - 0.011\,\mathrm{S}.$$

Although most of their spectra still exhibited asymmetric lines at 77 K, their field values were obtained by adjusting more Lorentzian lines to the spectra. In order to avoid this asymmetry to a large extent, Murad and Schwertmann [18] considered only the spectra at 4.2 K of 19 goethite samples with varying Al content, divided into three groups with different crystallinity. This resulted in the following equations:

$$B(4.2\ \mathrm{K}) = 50.54 - 3.3\,\mathrm{Al} - 0.0036\,\mathrm{S} \qquad (n = 19,\ R^2 = 0.967) \tag{1}$$

or

$$B(4.2\ \mathrm{K}) = 50.65 - 4.2\,\mathrm{Al} - 8.7\,\mathrm{MCD}(1\,1\,1)^{-1} \quad (n = 20,\ R^2 = 0.969). \tag{2}$$

Although both equations seem to be reliable ($R^2 \approx 0.97$) the sensitivity of B on both Al content and crystallinity is relatively low at very low temperatures. A thorough reinvestigation of these samples at 80 K, together with own-prepared relatively well-crystallized goethite series [19], has been carried out using a HFD fitting and introducing a linear correlation between the hyperfine field and the quadrupole shift. From such analyses the following relationships for B_p at 80 K have been obtained:

$$B_\mathrm{p}(80\ \mathrm{K}) = 50.31 - 8.9\,\mathrm{Al} - 0.0096\,\mathrm{S} \qquad (n = 26,\ R^2 = 0.96) \tag{3}$$

or

$$B_\mathrm{p}(80\ \mathrm{K}) = 50.55 - 10.8\,\mathrm{Al} - 20.8\,\mathrm{MCD}(1\,1\,1)^{-1} \quad (n = 26,\ R^2 = 0.96). \tag{4}$$

For the average hyperfine field an equation with even higher coefficients could be derived

$$B_\mathrm{av}(80\ \mathrm{K}) = 51.00 - 26.3\,\mathrm{Al} - 0.0228\,\mathrm{S} \quad (n = 26,\ R^2 = 0.94). \tag{5}$$

However, the higher sensitivity found for B_av with respect to B_p is more or less canceled out by the larger error in the determination of B_av. From all these equations it is clear that only one parameter can be estimated from the hyperfine field, whereas the other should be derived from complementary experiments.

In order to check the applicability of such equations, eq. (3) has been tested on an additional suite of eleven well-defined synthetic goethite samples with Al content varying between 0 and 28.8 at%. The spectra were fitted with a HFD in a similar way. The measured hyperfine field B_p has been compared with the value calculated from the known Al content and S and is displayed in figure 1(a). Although the field values differ only by a maximum of 2%, it gives rise to substantial errors in S or Al-content.

The electrical hyperfine parameters such as the quadrupole shift in the magnetically split spectrum and the quadrupole splitting in the high-temperature doublet are less influenced by Al substitution and crystallinity, which results in larger errors and smaller correlation coefficients [19]. For the most probable $2\varepsilon_\mathrm{Q}$ values, the following equations were found for the 80 K spectra:

$$\left|2\varepsilon_\mathrm{Q}(80\ \mathrm{K})_\mathrm{p}\right| = 0.247 + 0.14\,\mathrm{Al} - 13 \times 10^{-5}\,\mathrm{S} \qquad (n = 26,\ R^2 = 0.84), \tag{6}$$

$$\left|2\varepsilon_\mathrm{Q}(80\ \mathrm{K})_\mathrm{p}\right| = 0.250 + 0.12\,\mathrm{Al} - 0.28\,\mathrm{MCD}(1\,1\,1)^{-1} \quad (n = 26,\ R^2 = 0.84). \tag{7}$$

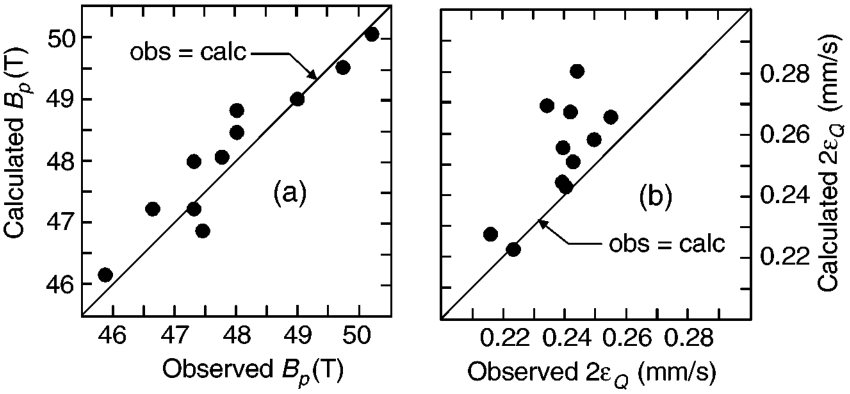

Figure 1. Observed and calculated most probable hyperfine field B_p (a) and quadrupole shift $2\varepsilon_\mathrm{Q}$ (b) by using eqs. (3) and (6), respectively, for a series of eleven Al goethite samples.

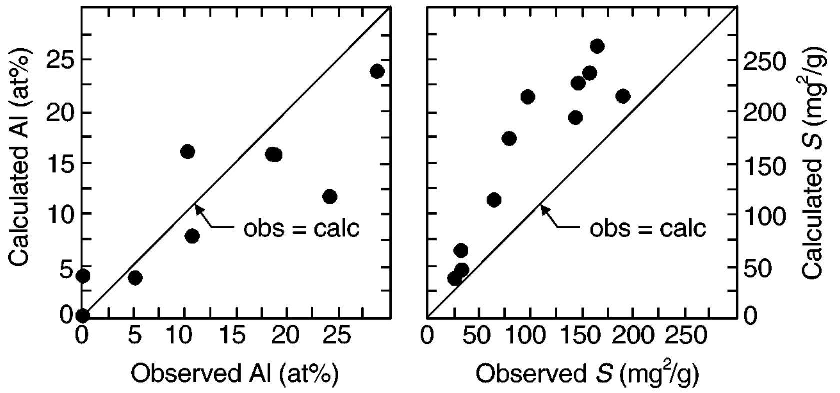

Figure 2. Observed vs. calculated Al content and specific surface S for the eleven Al goethite samples obtained from the most probable hyperfine field and quadrupole shift by combining eqs. (3) and (6).

For the quadrupole splitting at 400 K the correlation turned out to be much lower, i.e., $R^2 = 0.77$ for the average quadrupole splitting $(\Delta E_\mathrm{Q})_\mathrm{av}$ and even lower for the most probable one $(\Delta E_\mathrm{Q})_\mathrm{p}$ [20]. Equation (6) has been tested with the eleven aforementioned goethite samples, leading to strong deviations between the calculated and observed values (figure 1(b)).

In contrast to the hyperfine field, Al substitution and MCD have an opposite effect on the quadrupole shift. Therefore, it is tempting to derive both parameters from the combination of eqs. (3) and (6). The measured and calculated values for the Al content and surface area S obtained in this way are shown in figure 2. For the Al content the agreement is poor and the error amounts up to 50%. On the other hand, the calculated specific surface seems to be overestimated, but a better correlation is nevertheless observed.

Concerning the application to natural samples, Friedl and Schwertmann [21] have investigated 33 goethite samples from different origins, which, according to the formation conditions could be divided into 24 samples from tropical to subtropical soils and 9 samples from lake iron ores. The spectra were fitted using a split Gaussian distribution of Lorentzians from which the average hyperfine field was derived. The multiple correlation for the hyperfine field at 4 K for all samples yielded the following equation:

$$B_{\mathrm{av}}(4.2\ \mathrm{K}) = 50.38 - 5.46\,\mathrm{Al} - 3.39\,\mathrm{MCD}(1\,1\,1)^{-1} \quad (n = 33,\ R^2 = 0.779) \tag{8}$$

which is comparable to eq. (2) (Murad and Schwertmann [18]), although one must take into account that the determination of the hyperfine field value is slightly different. Comparison of the observed fields and the ones calculated according to eq. (2) results in significant deviations behaving somewhat differently for the goethite in tropical soils than for that in the lake ores [21]. This was corroborated by the linear regressions, separately obtained for the two kinds of samples, resulting in different coefficients for the Al content and MCD and hence implying some relationship with the formation conditions.

From the foregoing results it is clear that MS is still far from a reproducible analytical method to determine directly the structural properties of goethite. For the moment, it only enables to provide some crude indications with respect to either Al content or crystallinity, if one of the parameters is determined in some other way. The most probable reason for the observed deviations may reside in the assumption that the hyperfine parameters can be merely described by these two parameters. It is evident that other structural features, such as surface water, excess hydroxyl ΔOH and structural defects, all having some influence on the lattice parameters [22–24], will also play a substantial role in the magnitude of the hyperfine field and electrical interaction parameters. These additional structural parameters are mainly determined by goethite formation factors such as crystallization rate, temperature, OH concentration, etc., and are to some extent related to each other [22]. For instance, using ΔOH as an additional parameter in the multiple linear regression of $B_{\mathrm{p}}(80\ \mathrm{K})$ in our 26 samples improves significantly the correlation. Unfortunately, it can hardly be believed that the Mössbauer spectra, via the hyperfine parameters and their distributive effects, will contain enough information to unravel the structural parameters of goethite in complex natural samples.

3. Hematite: crystallinity, Al substitution and the Morin transition

Hematite is the most abundant iron oxide in soils and sediments. It particularly occurs in warmer climate regions in more or less close association with goethite. The particle size is usually small and isomorphous Al substitution for Fe is a common feature. Because of the high Néel temperature ($T_{\mathrm{N}} = 955$ K), and possibly a high effective anisotropy constant, the Mössbauer spectrum at RT appears as a sextet with a hyperfine field of about 50 T and a quadrupole shift of about -0.2 mm/s. Due to this high field, it can be readily distinguished even at RT from other iron oxides and hydroxides, making again MS to be a powerful method for identification purposes. For microcrystalline and Al-substituted hematite the spectra at RT often exhibit asymmetric lines, expected to be due to the same reasons as for goethite and are accordingly better fitted with a hyperfine-field distribution.

Similar to the case of goethite, some studies have been devoted to the search for the possibility of determining the Al content and particle size from the hyperfine parameters. From Mössbauer studies on Al hematite it was readily observed that the hyperfine field reduces by an amount 0.08–0.14 T per at% Al, depending on the preparation method [25–27]. It was assumed that also the particle size would play a role in the observed field value. Taking both MCD(0 0 1) and Al content into account, Murad and Schwertmann found the following equation [3,28]:

$$B(\mathrm{RT}) = 51.72 - 7.6\,\mathrm{Al} - 32/\mathrm{MCD}(0\,0\,1) \quad (n = 15,\ R^2 = 0.949) \tag{9}$$

which was obtained for Al concentrations in the region 0–10% Al.

Recently, a series of relatively well-crystallized hematite with Al up to 16 at% and with comparable particle size could be prepared by homogeneous precipitation of oxinates [29]. The following excellent correlation has been found for the field at RT:

$$B(\mathrm{RT}) = 51.65 - 6.08\,\mathrm{Al} \quad (n = 9,\ R^2 = 0.994) \tag{10}$$

demonstrating a lower Al dependence than previously found.

A series of six Al hematite samples have been prepared from decomposition of aluminous lepidocrocite (γ-[Fe,Al]OOH). Such samples are known to possess a relatively high Morin transition temperature [30,31] implying a lesser defect structure and a negligible OH content in comparison with wet-prepared hematite (see further). The hyperfine field values at RT have been calculated according to eq. (9) and are compared with the measured ones (figure 3). The calculated hyperfine fields turn out to be systematically lower than the observed values. This is also an indication of the

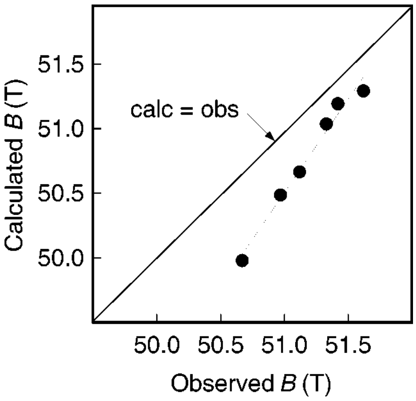

Figure 3. Observed vs. calculated hyperfine fields at RT using eq. (9) for a series of Al hematite samples prepared from Al lepidocrocite.

regression coefficients being too high (negative) in eq. (9). For the six lepidocrocite-derived samples the hyperfine field follows the equation

$$B(\mathrm{RT}) = 51.72 - 6.6\,\mathrm{Al} - 13/\mathrm{MCD}(0\,0\,1) \quad (n = 6,\ R^2 = 0.981).$$

From the foregoing there is a strong indication that the regression coefficients in the equations are dependent on the preparation method and therefore are rather bound to a particular suite of hematite samples. This will prevent us to estimate either the Al content or the particle size from the hyperfine field determined in unknown samples. Similar as for the field, equations have been proposed to express the variation of the quadrupole shift [28], the line widths [28] and even the Mössbauer fraction [32] with crystallinity and/or Al content. However, the larger errors in these parameters and the limited applicability of these equations, will make them even less significant.

Another more interesting feature could be the Morin transition in hematite, which is known to be very sensitive to cation substitutions and particle morphology [4]. Moreover, MS is a very suitable technique to probe this transition. Particularly, the large difference in the quadrupole shift $2\varepsilon_\mathrm{Q}$ between the weakly ferromagnetic ($\sim$(-0.19) mm/s) and the antiferromagnetic ($\sim$($+0.38$) mm/s) state is able to resolve accurately the spectra of the two phases, which occur simultaneously over a certain temperature range in non-ideal hematite. From the area fraction of both spectra vs.

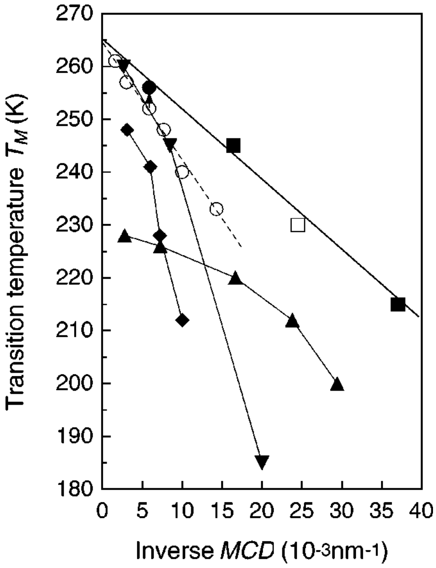

Figure 4. Morin transition temperatures T_M as a function of inverse MCD for different non-substituted hematite samples: (□) natural sample from Elba [33]; (■) prepared from decomposition of lepidocrocite above 500°C [30]; (▲) prepared from decomposition of goethite and thermal annealing at different temperatures up to 900°C [34]; (▼) prepared from ferric sulphate solution and annealed at temperatures up to 925°C [35]; (◆) prepared from metal hydrous oxid sols [36], and (○) afterwards heated at 300°C [36]. Due to a different definition, the latter T_M values are in fact not completely comparable. For one point (●) the value could be corrected, being more in line with those of lepidocrocite-derived hematite.

temperature, two quantities can be derived, i.e., the Morin-transition temperature T_M and the transition region ΔT_M, although the latter is difficult to define unequivocally.

Figure 4 displays a collection of previously published T_M for different non-substituted hematite samples as a function of the inverse MCD. The spread in T_M clearly illustrates that the Morin transition is not solely dependent on the particle size. Particularly, in goethite-derived hematite the transition temperature after annealing at high temperatures still remains low although the MCD is relatively high [34]. On the other hand, the samples prepared via the lepidocrocite-maghemite channel have a very high T_M ($>$215 K) even for very small particle sizes (61 and 27 nm) [30], inferring that these hematites contain less defects and negligible OH than those derived from goethite. These results are in line with those of a recent work of Dang et al. [35] in which two series of hematite, prepared in different ways and annealed at several temperatures have been investigated. They derived that the lack of the occurrence of the Morin transition down to 4 K is rather related to the lattice parameters, which in turn are determined by incorporated water and OH groups [37]. Considering the additional factors influencing the Morin transition, such as intrinsic particle size effects, surface effects [38] and various possible isomorphous substitutions (Al, Mn, Ti, . . .), it becomes obvious that the determination of the transition features alone cannot give any clear-cut information about the sample characteristics.

4. Magnetite/maghemite: nonstoichiometry or mixtures

The origin of magnetite (Fe_3O_4) in soils is usually lithogenic, but fine-coarse pedogenic magnetite has now been established to be present as well [39]. Maghemite (γ-Fe_2O_3) is commonly formed by oxidation of lithogenic magnetite, however, its abundance in tropical and subtropical regions can also be explained, for instance, by the conversion of goethite through fires under certain reducing conditions. Both kinds of maghemites are different in composition in the sense that the first may contain some Ti, whereas in the second, Al substitution is more common. Maghemite, being the fully oxidized counterpart of magnetite, can coexist with the latter, because smaller Fe_3O_4 crystals are easier transformed to γ-Fe_2O_3 than the coarser ones. However, it can also occur simultaneously with magnetite from a different origin [40]. On the other hand, the intermediate stages of magnetite oxidation result in nonstoichiometric oxides and most of the natural magnetite in soils actually seems to be partly oxidized. It is generally a problem how to distinguish between nonstoichiometric magnetite and magnetite/maghemite mixtures because X-ray diffraction results are not evident in that respect.

Magnetite has the following structural formula

$$\left(\mathrm{Fe}^{3+}\right)_\mathrm{A}\left[\mathrm{Fe}^{2.5+}\right]_\mathrm{B}\mathrm{O}_4$$

in which the octahedral-(B$-$)site ferrous and ferric ions merge into $Fe^{2.5+}$ due to a fast electron hopping above the Verwey transition ($>$125 K). In the Mössbauer spectra at

Table 1
Hyperfine parameters of magnetite and maghemite at RT. All quadrupole shifts are close to zero.

Oxide	Valence and site	B_{hf} (T)	δ_{Fe} (mm/s)	Area ratio	Ref.
Fe_3O_4	$(Fe^{3+})_A$	~49.1	0.28	1	
	$(Fe^{2.5+})_B$	~46.0	0.66	~1.9	
$Fe_{3-x}O_4$	$(Fe^{3+})_B$	49.8–50.6	0.39		[45]
γ-Fe_2O_3	$(Fe^{3+})_A$	49.8	0.24	1	[46]
	$(Fe^{3+})_B$	49.8	0.36	~1.66	[46]

RT this cation repartition results in the two[1] well-known distinct sextets with typical hyperfine parameters for Fe^{3+} and $Fe^{2.5+}$ (table 1), and with an area ratio of about 1 : 1.9 for stoichiometric magnetite.

Nonstoichiometric magnetite has the general formula $Fe_{3-x}O_4$ with $0 < x < 0.33$. If the vacancies are supposed to be merely located on the octahedral sites in the spinel structure, the formula can be written as

$$\left(\mathrm{Fe}^{3+}\right)_{\mathrm{A}}\left[\mathrm{Fe}^{2+}_{1-3x}\mathrm{Fe}^{3+}_{1+2x}\square_x\right]_{\mathrm{B}}\mathrm{O}_4.$$

The fast electron hopping, which is known to be a pair-localized phenomenon in magnetite [42], results in $Fe^{2.5+}$ by an equal amount of octahedral Fe^{2+} and Fe^{3+}, yielding the following formula:

$$\left(\mathrm{Fe}^{3+}\right)_{\mathrm{A}}\left[\mathrm{Fe}^{2.5+}_{2(1-3x)}\mathrm{Fe}^{3+}_{5x}\square_x\right]_{\mathrm{B}}\mathrm{O}_4.$$

The Mössbauer spectrum contains now three sextets: one for $Fe^{2.5+}$ and two for Fe^{3+}, the latter with slightly different isomer shifts and hyperfine fields (table 1). This practically results in a similar spectrum as for stoichiometric magnetite, however, with a different area ratio for the subspectra. Maghemite, as the end member of nonstoichiometric magnetite ($x = 0.33$), has the general formula

$$\left(\mathrm{Fe}^{3+}\right)_{\mathrm{A}}\left[\mathrm{Fe}^{3+}_{5/3}\square_{1/3}\right]_{\mathrm{B}}\mathrm{O}_4.$$

The corresponding Mössbauer spectrum consists now of two Fe^{3+} sextets with hyperfine parameters which are very similar to those of Fe^{3+} in nonstoichiometric maghemite (table 1). Magnetite/maghemite mixtures as well as nonstoichiometric magnetite will, therefore, result in completely similar spectra consisting of one $(Fe^{2.5+})_B$, one $(Fe^{3+})_A$ and one $(Fe^{3+})_B$ sextet. Although the latter two can be easily resolved by applying an external field, there will be no significant difference between nonstoichiometry and mixtures as has been recently shown experimentally [43]. Moreover, unknown Al or Ti substitution for Fe in natural samples will make any measurable minor difference in the hyperfine parameters useless. So, in contrast to what often has been claimed [44],

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[1] In fact, there are three sextets because the $Fe^{2.5+}$ yields two sextets due to two possible directions of the EFG principal axis with respect to that of the hyperfine field [41]. However, for most purposes a two-sextet fitting is adequate.

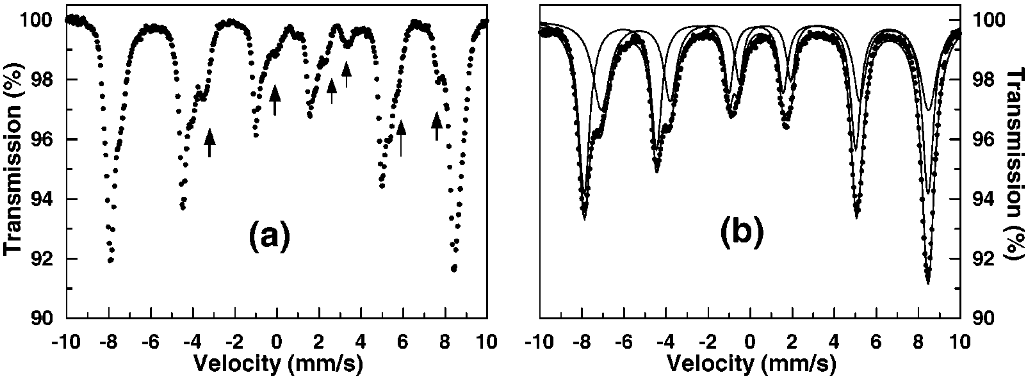

Figure 5. (a) Spectrum of stoichiometric magnetite at 100 K with visible Fe^{2+} lines (indicated by arrows), and (b) spectrum of nonstoichiometric magnetite $Fe_{2.944}O_4$ at 100 K with the two typical Fe^{3+} and $Fe^{2.5+}$ sextets.

MS at RT is not able to distinguish between nonstoichiometric magnetite and magnetite/maghemite mixtures, even by using an applied field. This is, of course, only true for bulk oxides because microcrystalline maghemite is readily distinguished from bulk magnetite or nonstoichiometric magnetite through a spectrum with lower hyperfine fields (and with asymmetric lines) and/or the presence of a superparamagnetic doublet.

Another feature, which could enable to distinguish between nonstoichiometry and mixtures, is the Verwey transition. In stoichiometric magnetite this transition is known to occur at 125 K and results at lower temperatures in a complex spectrum, showing at least five sextets to be present [47–49]. Nevertheless, this transition is readily recognized by the presence of several absorption lines typical for Fe^{2+} below the transition temperature T_V. Because T_V strongly depends on the magnetite stoichiometry [50], the spectral behavior just below 125 K will, therefore, be quite different. Figure 5(a) displays the spectrum of stoichiometric magnetite at 100 K exhibiting some typical Fe^{2+} contributions (indicated with arrows). This spectrum is clearly different from that of a nonstoichiometric magnetite with formula $Fe_{2.944}O_4$, being still above T_V at 100 K (figure 5(b)). So, visual inspection of the spectral behavior just below 125 K yields some potential to discern between nonstoichiometric magnetite and magnetite/maghemite mixtures. In fact, this difference can also be visualized by thermoscan measurements at about zero velocity below T_V [51].

Unfortunately, there are a few drawbacks in this method for practical application in natural samples. Firstly, this procedure becomes more difficult if small-particle materials with asymmetric lines are involved. This has been clearly illustrated in the MS characterization of iron oxides produced by bacteria [52]. Moreover, all kinds of substitutions in natural magnetite, such as Ti, will also alter the Verwey transition significantly [53,54]. Combined with a possible range of nonstoichiometry, this will render this procedure impracticable.

5. Conclusions

Mössbauer spectroscopy has proved to be a valuable tool with respect to direct identification and quantification of iron oxides and (oxy)hydroxides in clays and sediments. However, it has only a limited potential for further characterization such as the determination of Al content, crystallinity, stoichiometry, etc. The main reason for this resides in the hyperfine parameters being dependent on much more structural properties than Al content and crystallinity alone. This is demonstrated by the variation of the regression coefficients in the equations for B of goethite and hematite according to the preparation method for synthetic samples or to the origin in the case of natural samples. However, comparison of the Mössbauer spectra of samples, formed under the same conditions, could yield some qualitative results, but more systematic studies on series of well-characterized natural samples from different selected origins are needed. Moreover, the fitting procedure of the hyperfine-field distributed spectra should be standardized in order to use comparable hyperfine parameters. It is also demonstrated that the Morin transition in hematite is too sensitive to other structural parameters such as incorporated water and OH in order to provide valuable information about particle size or Al substitution. Finally, MS is not able to distinguish between nonstoichiometric magnetite and magnetite–maghemite mixtures, even by applying external fields. Also, probing the Verwey transition is of limited validity in that respect for natural samples.

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