American Mineralogist, Volume 67, pages 1007–1011, 1982

The characterization of goethite by Mössbauer spectroscopy

ENVER MURAD

Lehrstuhl für Bodenkunde, Technische Universität München
D-8050 Freising-Weihenstephan, Federal Republic of Germany

Abstract

Room temperature Mössbauer spectra of goethite often have excessively wide and asymmetric resonant lines, which are adverse to computer-fitting using Lorentzian functions. When distributions of Lorentzians, corresponding to distributions of magnetic hyperfine fields, are fitted to such spectra, rational and reproducible fits ensue. The hyperfine field at which a spectrum shows maximum absorption and the half widths of the hyperfine field distribution to the left and right of this hyperfine field give measures for the quality of crystallinity and deviations from stoichiometry and/or crystalline perfection. This technique can be used to characterize both room temperature spectra and spectra taken, where necessary to induce magnetic hyperfine splitting, at lower temperatures.

Introduction

At room temperature well crystallized, chemically pure goethites (α-FeOOH) show magnetically split Mössbauer spectra. Minor deviations from ideal crystallinity or chemical purity, however, cause noticeable broadening of the resonant lines. When such spectra are fitted with a set of six Lorentzian lines, divergences between the experimental data and the computed fits ensue. These divergences become the more pronounced the less perfect the crystals are. As isomorphous substitutions and/or defects increase and particle sizes decrease, a simple one-sextet model will no longer satisfactorily fit the spectrum (Murad, 1979). At particle sizes below about 200Å and/or considerable substitution of other elements (*e.g.* Al) for Fe, magnetic ordering at ambient temperature disappears totally, and the spectrum consists of a paramagnetic doublet (Kraan and Loef, 1966; Janot and Gibert, 1970).

Stoichiometric goethite is practically non-existent in nature. Most room temperature Mössbauer spectra of natural goethites therefore, if at all magnetically ordered, show broadened resonant lines, or are essentially superparamagnetic (Janot *et al.*, 1968; Govaert *et al.*, 1976; Murad, 1979). The broadened resonant maxima become narrower, and many samples that have superparamagnetic spectra at room temperature show magnetic hyperfine splitting when cooled by liquid nitrogen. For extremely poorly crystallized and highly substituted goethites (*e.g.* most pedogenic goethites) liquid helium is necessary.

The purpose of this paper is to quantitatively characterize Mössbauer spectra of goethites which have non-Lorentzian lines due to small particle size, imperfect crystallinity, and/or deviations from stoichiometry.

Experimental

Mössbauer spectra of over 70 synthetic and natural goethites of different particle sizes and chemical purity were run at temperatures between 300 and 4 K. Instrumental and procedural details are as described by Murad and Schwertmann (1980). The iron oxide mineralogy of all samples was monitored by X-ray diffraction to ascertain the identity of all components which could possibly contribute to the Mössbauer spectra.

About 25 of the goethite spectra were fitted with sets of up to 30 superposed sextets, whose hyperfine fields varied in steps of 15 kOe. The line widths of these sextets were fixed at 0.30 mm·s^{-1}, which is slightly less than the value observed for pure, bulk hematite. The assumption was made that isomer shift and quadrupole splitting are not affected by the crystalline imperfections, so that these parameters are the same for all the constituent sextets. The average isomer shifts, quadrupole splittings, and intensities of up to 15 component sextets were allowed to vary freely. The hyperfine field distributions were plotted as histograms with class intervals of 15 kOe.

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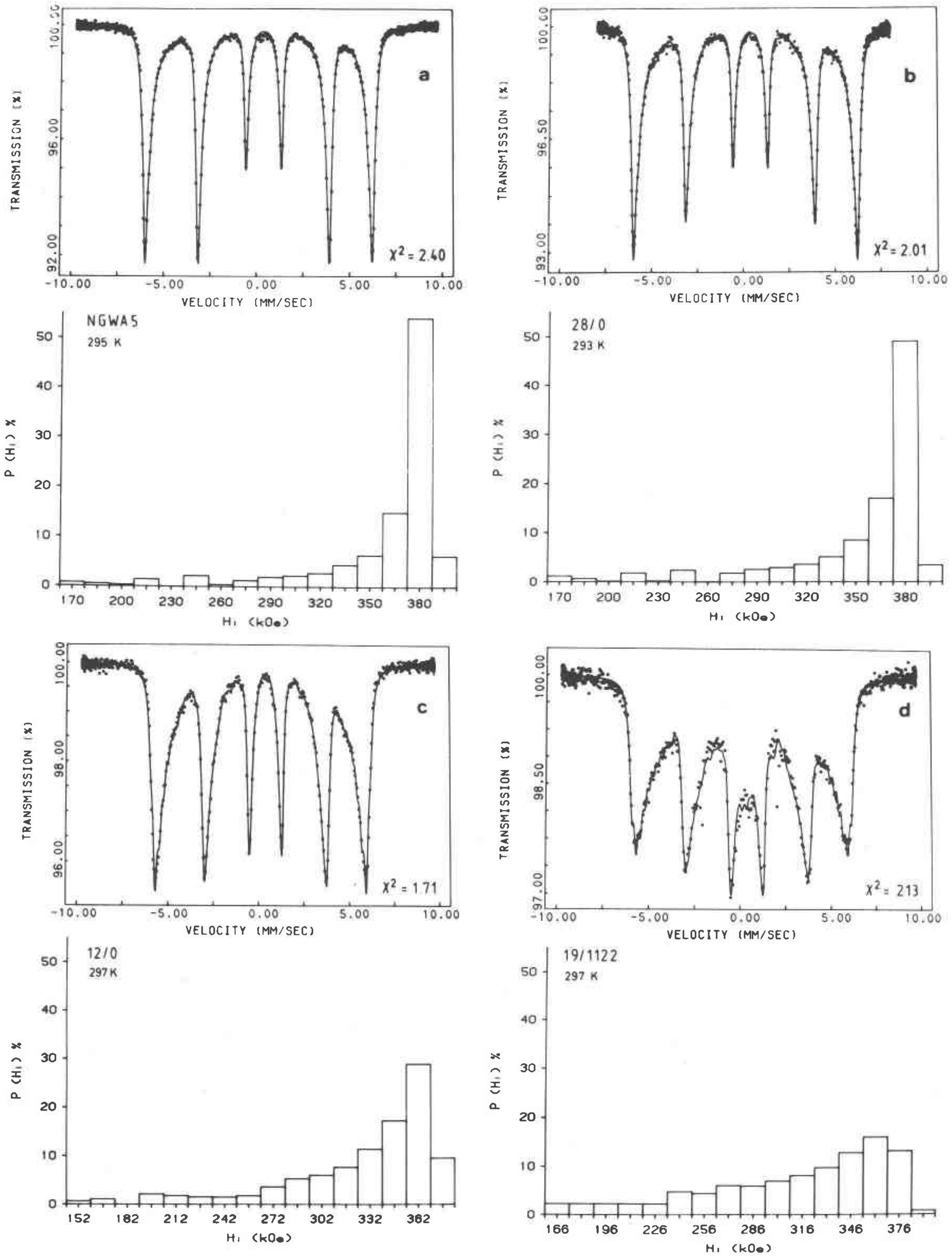

Fig. 1. Room temperature Mössbauer spectra and corresponding hyperfine field distributions of three chemically pure and one Si doped goethite. Widths of hyperfine field distributions increase and master class fields decrease from 1a to d; the left and right half widths (and master classes) are 10 and 8 (380), 11 and 8 (380), 22 and 11 (362), and 45 and 21 (361) kOe, respectively. The increased intensity of lines 2 and 5 in sample NGWA5 (Fig. 1a) results from preferred orientation of the goethite fibres perpendicular to the gamma rays.

The hyperfine field class with the highest probability, *i.e.* that hyperfine field at which the Mössbauer spectrum shows maximum absorption, was usually determined graphically. For room temperature spectra which are sufficiently well developed to permit characterization by the described method, this "master class" lies between 380 and about 340 kOe. The intensities of the constituent sextets of each distribution were computed in 15 kOe intervals from the "master class" of the sample. All other iron oxides that show magnetic ordering at room temperature (hematite, maghemite, feroxyhite and magnetite) have higher hyperfine fields, so that these will not contribute to the hyperfine field distributions of goethite, which are spread *downwards* from 380 kOe.

Details pertaining to the preparation of selected synthetic samples, whose spectra are depicted in Figures 1 and 2, and the quality of crystallinity of these, are given in Table 1.

Table 1. Properties of goethites whose Mössbauer spectra are shown in Figures 1 and 2

Sample No.	Type N/S	Method of preparation or provenance	Fe_o/Fe_t	Surface area m^2/g	WHH 110
NGWA5	N	Western Australia	n.d.	n.d.	0.10
28/0	S	Transformation of ferrihydrite in 0.4M KOH at 70°C for 14 days	<0.005	30	0.34
12/0	S	Transformation of ferrihydrite in 2M KOH at 70°C for 8 days	<0.001	88	0.96
19/1122	S	Transformation of lepidocrocite in 2M KOH — $1.23 \cdot 10^{-4}$M Si mixed solution at room temperature	0.037	89	0.65
P147	S	Oxidation of a 0.05M $FeCl_2$ solution with O_2 + CO_2 at pH 6-7 and room temperature	0.051	167	1.29

Type : N = Natural; S = Synthetic sample
Fe_o/Fe_t = Ratio of oxalate extractable to total iron
WHH 110 = Width at half height of 110 X-ray diffraction peak (°2θ) corrected for instrumental broadening.

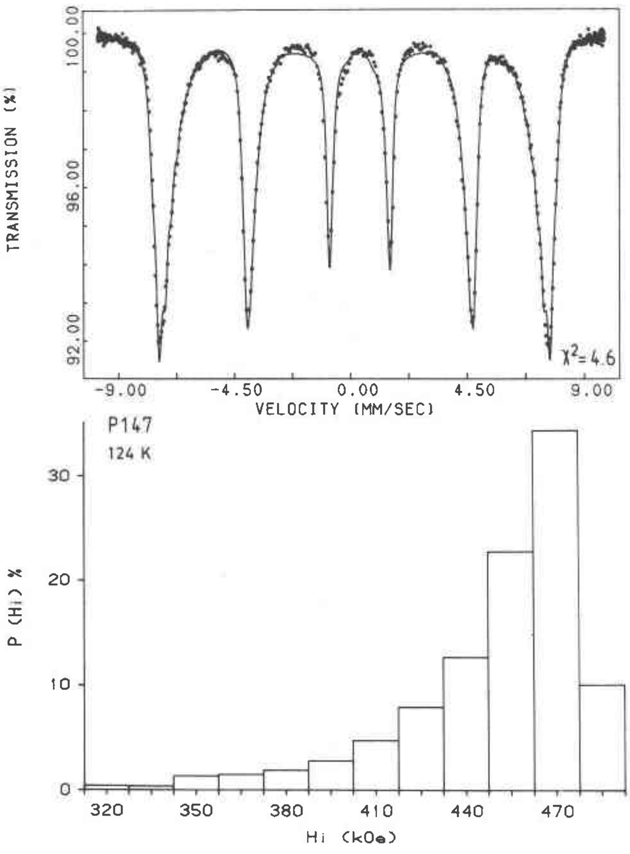

Fig. 2. Mössbauer spectrum and hyperfine field distribution of a chemically pure, synthetic goethite of extremely small particle size (MCD parallel [110] = 7 nm) at 124 K.

Results

At room temperature the hyperfine field distributions comprise one or two classes at higher fields and up to 24 classes at lower fields than the master class. The hyperfine field probabilities tend to become erratic as the outer peaks of lower field classes come to lie under the second and fifth peaks of the composite spectrum, *i.e.* at about 2/3 the hyperfine field of the master class (Fig. 1). Well developed spectra have no significant contributions of lower hyperfine fields, so that the histograms can be cut off this stage (Fig. 1a).

Poorly crystallized goethites, however, have significant contributions of lower fields (Fig. 1b, c), even down to 0 kOe (*ca.* 1.5% absorption near ±0 mm s^{-1} in Fig. 1d). To avoid erratic variations in the populations of classes of hyperfine fields below 2/3 that of the master class in such goethites, it proved necessary to place the populations of these in some systematic relation to one another. A simple but effective model assumes contributions to the spectrum from the 11th class below the master class downwards to vary linearly, the population of each class differing from that of the preceding one by a constant. This incremental factor is also determined by the fitting procedure. This technique allows a satisfactory fit to be made where contributions of low hyperfine fields are noticeable, while avoiding erratic variations in class population.

Useful numeric parameters to describe the hyperfine field distributions are the half widths of these distributions to the left (*i.e.* towards lower fields) and right (towards higher fields) of the master class. Figures 1a, b, and c show Mössbauer spectra of chemically pure goethites whose particle sizes decrease in this order (Table 1). These spectra show that a particle size reduction beyond about 25 nm parallel [110] (calculated from the width at half height of the X-ray diffraction peak using the Scherrer formula) results in lower master class hyperfine fields and wider distributions, *i.e.* in higher contributions of lower hyperfine fields to the distributions.

The effects of atomic substitution on the Mössbauer spectrum of goethite are quite similar. Room temperature Mössbauer spectra of goethites with Al-substitutions of up to 5% can, for example, be adequately fitted by the same procedure. Doping even with minor amounts of Si also has a similar influence on the Mössbauer spectra of this mineral (Fig. 1d).

The distribution curves become narrower as absorber temperatures are lowered. Mössbauer spectra of samples which are superparamagnetic at room temperature (due to small particle size or a high degree of isomorphous substitution) also tend to order magnetically as temperatures are lowered. Spectra of such samples, however, even when magnetically split at liquid nitrogen temperature, often enough still show deviations from Lorentzian line shape (Goodman and Lewis, 1981). The technique described above can thus also be applied to their study (see Fig. 2).

Goethites of very poor crystallinity and noticeable substitution, *e.g.* most pedogenic goethites (Simopoulos *et al.*, 1975; Schwertmann *et al.*, 1982a) require even lower temperatures to order magnetically. At 4 K, however, the Mössbauer spectra of all studied goethites showed complete magnetic ordering. At this temperature line widths still varied somewhat, but were usually not excessive; left + right half widths of the hyperfine field distributions usually lay around 22 kOe and were only occasionally higher (Schwertmann *et al.*, 1982b).

Discussion

The described poor quality of the Mössbauer spectra of goethite doubtlessly results from the low Néel temperature of this mineral. For pure goethite the Néel temperature lies at *ca.* 400 K (Woude and Dekker, 1966; Forsyth *et al.*, 1968), so that under ambient conditions the reduced temperature T/T_N is approximately 0.75. Deviations from stoichiometry lower the Néel temperature, thus increasing this ratio further. At high substitutions (*e.g.* >10% Al for Fe) the Néel temperature of goethite lies beneath room temperature, so that the samples become paramagnetic and the spectra consist of a quadrupole split doublet.

At room temperature the magnetic hyperfine field will be lowered by non-stoichiometry (Dézsi and Fodor, 1966; Janot *et al.*, 1968; Hogg *et al.*, 1975), very small particle size (Kraan and Loef, 1966; Yamamoto, 1968), and, probably, structural defects. Such deviations from crystalline perfection can also be expected to lower the saturation hyperfine field at 0 K, though to a lesser extent.

Broadening of absorption peaks in imperfectly crystallized goethite has been attributed to an interruption of the antiferromagnetic coupling in the crystallographic **c**-direction (Woude and Dekker, 1966). This can result in a partial or complete breakdown of the hyperfine structure of apparently well-crystallized goethites below the Néel temperature. Such interruptions can be brought about by the effects mentioned above, or by combinations of these (*e.g.* substitution of Al for Fe *plus* small particle size; Golden *et al.*, 1979).

Both natural and synthetic goethites can be assumed, in any one sample, not to form particles of one uniform size, but rather a range of particle sizes with one or more maxima. Fluctuations in the distribution of foreign atoms substituting for Fe will, similarly, give rise to locally different chemical environments and Néel temperatures.

Variations of particle size (Mørup *et al.*, 1976) and locally different degrees of chemical substitution in non-stoichiometric samples will therefore result in the development not of a discrete magnetic hyperfine field, but rather in a superposition of different fields, *i.e.* in a distribution of hyperfine fields. The highest field which can conceivably contribute to such a distribution is that of a perfectly crystallized, stoichiometrically composed crystal: *ca.* 382 kOe for goethite at 295 K. The hyperfine field distributions will be skewed downwards from this limiting value towards lower fields, giving the typical asymmetrically broadened resonant lines.

Decreasing the absorber temperature leads to a lower reduced temperature, at which relaxation effects and variations of the Néel temperature will no longer have as pronounced an influence as at room temperature. At liquid nitrogen temperature hyperfine field distributions of significant widths are therefore observed only for goethites which have paramagnetic or superparamagnetic Mössbauer spectra at room temperature (Fig. 2).

The fitting of distributions of static hyperfine fields to the spectra represents a pragmatic approach to the problem of characterizing Mössbauer spectra of goethite, but should not be taken as implying the total absence of relaxation phenomena. Spectra observed for goethite (*e.g.* those shown in Figs. 1a to c and 2), however, often differ from relaxation model calculations (Wickman, 1966), indicating that hyperfine field distributions do indeed play a major role in the asymmetric broadening of goethite lines. The left and right half widths and master class hyperfine field introduced in this paper represent rational and reproducible "distribution parameters" suitable for the characterization of goethites of different crystallinites by Mössbauer spectroscopy.

Acknowledgments

I am indebted to U. Schwertmann and D. G. Schulze (Lehrstuhl für Bodenkunde in Freising) for placing the X-ray and analytical data given in Table 1 at my disposal and to F. E. Wagner (Physik Department, Technische Universität München in Garching) for making the measurements at 120 and 4 K possible. U. Schwertmann and F. E. Wagner provided helpful reviews of the manuscript. This study has been supported by the Deutsche Forschungsgemeinschaft.

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Manuscript received, February 18, 1982;
accepted for publication, May 7, 1982.