

Magnetic ordering in Al-rich goethites: Influence of crystallinity

ENVER MURAD,* LAWRENCE H. BOWEN

Department of Chemistry, North Carolina State University,
Raleigh, North Carolina 27695-8204, U.S.A.

ABSTRACT

Mössbauer spectra of two highly Al-substituted goethites of different crystallinities were taken between room temperature and 4.2 K. Between 4.2 and 100 K, both samples show similar variations of magnetic hyperfine fields, which decrease approximately linearly from maxima of about 49.1 T at 4.2 K. In both samples, magnetically ordered and paramagnetic components coexist over wide—but different—temperature ranges. The differences in the magnetic ordering patterns are attributed to the influences of local compositional inhomogeneities and sample crystallinities. The onset of magnetic order is not marked by one well-defined Néel temperature; compositional variations on an atomic scale lead to a range of Néel temperatures. Superimposed upon this variation, superparamagnetic relaxation can lower magnetic blocking temperatures of poorly crystallized goethites. Poorly crystallized Al-rich goethites may have to be cooled down to temperatures significantly below 77 K to attain complete magnetic order.

INTRODUCTION

Goethite (α -FeOOH) has an orthorhombic structure in which Fe^{3+} occupies the $4c$ sites of space group $Pbnm$. Pure goethite of bulk crystallinity orders antiferromagnetically at a Néel temperature of about 400 K (van der Woude and Dekker, 1966; Forsyth et al., 1968; Mørup et al., 1983; DeGrave and Vandenberghe, 1986). The static magnetic hyperfine field developed below this transition approximately follows a Brillouin function and amounts to about 38 T at room temperature, 50 T at 77 K, and 50.6 T at 4.2 K.

Al can substitute up to an extent of about 33 mol% for Fe in goethite (Schwertmann, 1985). This substitution of a diamagnetic ion (Al^{3+}) for a paramagnetic ion (Fe^{3+}) reduces magnetic interactions and thereby lowers both the Néel temperature and the saturation hyperfine field.

The influence of Al substitution on the Mössbauer spectrum of goethite was first described by Janot and Gilbert (1970). About 12 mol% Al substitution is sufficient to lower the Néel temperature of goethite below room temperature (Fleisch et al., 1980) and to reduce the saturation hyperfine field by 0.50 T (Murad and Schwertmann, 1983).

As particles become smaller, their specific surface area increases, and consequently surface phenomena attain more importance. Crystal surfaces, however, can be considered "huge defects," and themselves introduce further defects into the interior of crystals (Schroeder, 1970). As

a result of the high surface areas of microcrystals, a distinction between effects of particle size and those of crystal defects becomes increasingly obscured as particle sizes decrease in the microcrystal range. For the materials studied here (at least for the more finely grained goethite), the term "crystallinity" is therefore used in the general sense that deviations from crystalline perfection effect observable changes in physical behavior (e.g., X-ray diffraction-line broadening) which, however, cannot be unequivocally related to either particle-size reduction or structural defects.

In poorly crystallized material, superparamagnetic relaxation can lower the onset of magnetic order to temperatures below the Néel temperature and reduce magnetic hyperfine fields at all temperatures. Crystal-size reduction may thus effect changes in the magnetic properties that qualitatively resemble those of Al substitution (Golden et al., 1979). Fysh and Clark (1982) attributed lower magnetic hyperfine fields observed for goethites of small particle size to superparamagnetism, indicating that this hyperfine-field reduction should be absent at adequately low temperatures. Murad and Schwertmann (1983), however, showed this effect to extend down to 4.2 K and thus to be at least in part due to reduced hyperfine-field supertransfer. If a hyperfine field lower than 50.6 T is observed for a goethite at a temperature below about 50 K, the hyperfine-field reduction therefore cannot be interpreted exclusively in terms of an Al substitution—as has been occasionally done in the past—unless an influence of crystallinity can be positively ruled out.

One Mössbauer spectrum—even if taken at a very low temperature—is therefore not sufficient to characterize

* Permanent address: Lehrstuhl für Bodenkunde, Technische Universität München, D-8050 Freising-Weihenstephan, Federal Republic of Germany.

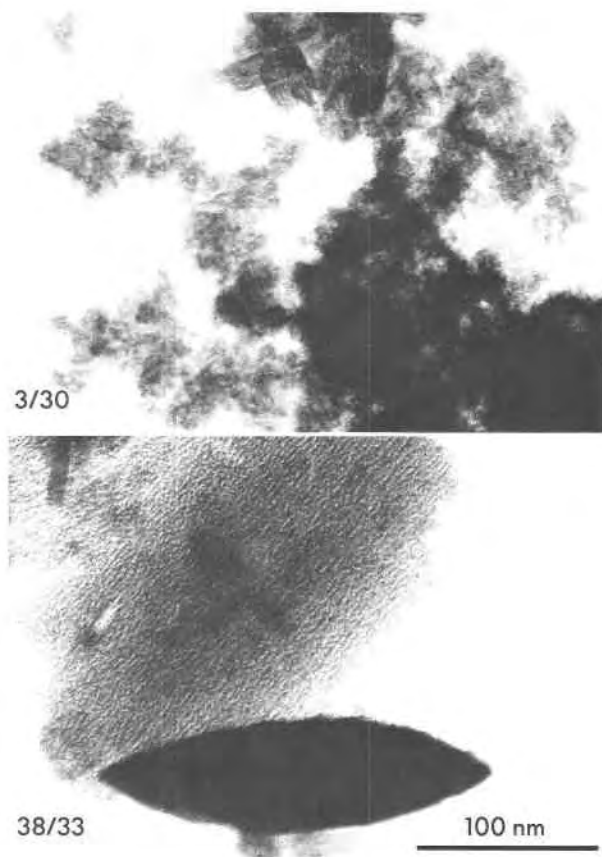


Fig. 1. Transmission-electron micrographs of goethites 3/30 and 38/33. Both micrographs at the same magnification (given by scale bar).

adequately an aluminous goethite of poor crystallinity. The variations of magnetic properties as a function of temperature as shown by Mössbauer spectra may, however, present additional evidence for this purpose. In the present study Mössbauer spectra of two Al-rich goethites of markedly different crystal sizes were taken at different temperatures to study the influence of Al substitution and crystallinity on the magnetic properties of such samples.

EXPERIMENTAL METHOD

Sample 38/33 was prepared by storing a mixture of 0.05 *M* FeCl₂ and 0.025 *M* AlCl₃ solutions at pH 11.7 and room temperature in a stoppered bottle. This was opened and shaken daily, thus giving limited exposure to air for Fe²⁺ oxidation. After 94 d the precipitate—mostly goethite—was washed free of salts and, to remove minor amounts of coprecipitated magnetite, treated for ca. 2 h with 1.8 *M* H₂SO₄ at room temperature.

Sample 3/30 was prepared by mixing a solution containing 0.014 *M* FeCl₂ and 0.006 *M* AlCl₃ with an excess of 0.005 *M* NaHCO₃ (Goodman and Lewis, 1981). Air was bubbled through this mixture at room temperature and pH 7–9 for 48 h, after which the precipitate formed was washed free of salts and dried. To remove coprecipitated ferrihydrite, the sample was subjected to three consecutive treatments with acid ammonium oxalate (Schwertmann, 1964). This sample is the Al-rich endmember of

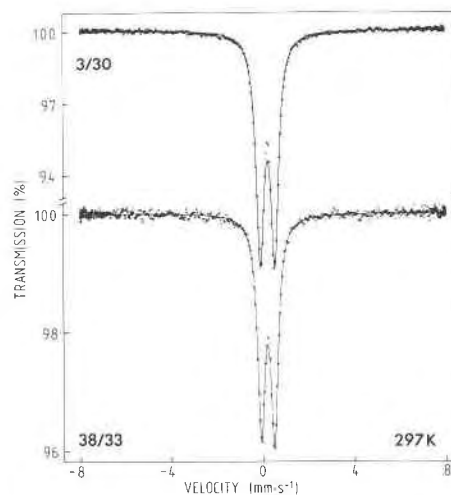


Fig. 2. Room temperature Mössbauer spectra of goethites 3/30 and 38/33 fitted with one doublet.

the goethites of synthesis series 3 and 4 studied at 4.2 K by Murad and Schwertmann (1983).

For chemical analyses, the samples were digested in concentrated HCl. The Fe content of 38/33 was determined colorimetrically using sulfosalicylic acid, and that of 3/30 by atomic absorption (AAS). The Al content of 38/33 was determined both colorimetrically using aluminon and by AAS and that of 3/30 by AAS following dissolution with Na dithionite (Mehra and Jackson, 1960).

The samples were further characterized by X-ray powder diffraction using CoK α radiation on a Philips PW 1130 unit equipped with a diffracted-beam graphite monochromator, ethylene glycol monoethyl ether (EGME) surface-area measurements, and transmission electron microscopy using a Zeiss EM10 instrument operated at 80 kV.

The majority of Mössbauer spectra were taken with a microprocessor-controlled system described by DeGrave et al. (1982). The system comprised a ca. 50 mCi ⁵⁷Co-Rh source mounted on a drive system operated in the sawtooth mode, with a He-Ne laser interferometer providing velocity calibration. The absorbers were cooled to temperatures between 180 and 13 K in a Displex closed-cycle cryostat. Radiation data recorded with a proportional counter and laser data were collected simultaneously and stored in different sections of the microcomputer memory (1024 channels each). Adjacent velocity points were averaged to provide 432 data points for the analysis. Spectra were run for an average time of 24 h and analyzed using an IBM 3081 computer by fitting Lorentzian line shapes to the resonant lines. Selected spectra were also analyzed using a modified version (Amarasiriwardena et al., 1986) of the Wivel and Mørup (1980) hyperfine-field distribution program. Supplementary Mössbauer spectra were taken at room temperature and with both the absorber and source cooled down to 78 and 4.2 K in a bath cryostat.

RESULTS

The different crystal sizes of the two samples are apparent from the electron micrographs. These show 38/33 to consist of relatively well-developed cigar-shaped to platy crystals, about 200 nm long and 40 nm wide, where-

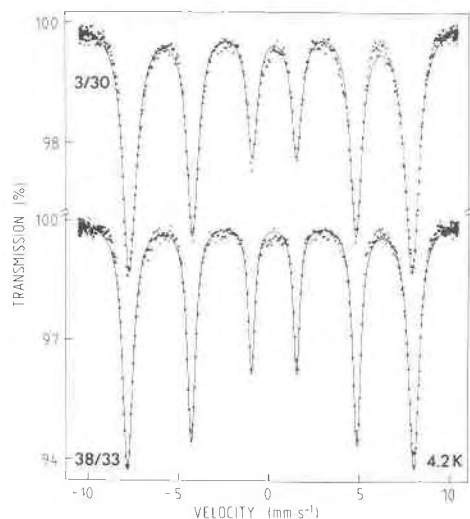


Fig. 3. Mössbauer spectra of goethites 3/30 and 38/33 at 4.2 K fitted with one sextet.

as almost no particle morphology is evident for 3/30 (Fig. 1).

X-ray diffraction showed both samples to consist exclusively of aluminous goethite. The chemical analyses showed a molar Al substitution, $Al_s = Al/(Al + Fe)$, of 0.306 for sample 38/33 and 0.255 for sample 3/30.

X-ray line widths indicate 38/33 to have a mean crystallite dimension in the [111] direction (MCD_{111}) of 74 nm, whereas 3/30 had an MCD_{111} of only 9 nm. The surface areas S of $35 \text{ m}^2 \cdot \text{g}^{-1}$ (38/33) and $328 \text{ m}^2 \cdot \text{g}^{-1}$ (3/30) are in agreement with the differences in particle size observed by electron microscopy and X-ray diffraction.

At room temperature, both samples were paramagnetic (Fig. 2). Mössbauer spectra taken in an expanded velocity range showed these to have similar isomer shifts of 0.35

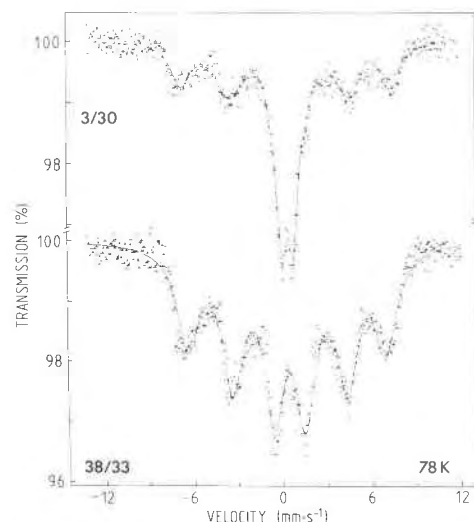


Fig. 4. Mössbauer spectra of goethites 3/30 and 38/33 at 78 K. Magnetically ordered components fitted with one sextet each.

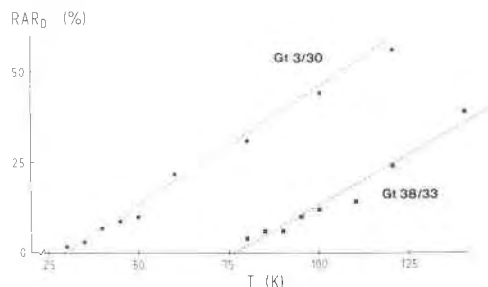


Fig. 5. Relative areas of doublet components (RAR_D) in the Mössbauer spectra of goethites 3/30 and 38/33 between 25 and 150 K.

$\text{mm} \cdot \text{s}^{-1}$ relative to metallic Fe, typical for high-spin Fe^{3+} in octahedral coordination. 38/33 had a relatively high quadrupole splitting of $0.57 \text{ mm} \cdot \text{s}^{-1}$ and 3/30 an even higher quadrupole splitting of $0.62 \text{ mm} \cdot \text{s}^{-1}$.

At 4.2 K, both samples showed complete magnetic order, with rather wide resonant lines (Fig. 3). One-sextet fits gave quite similar magnetic hyperfine fields of 49.2 T for 38/33 and 48.9 T for 3/30. Because both Al substitution and poor crystallinity can reduce magnetic hyperfine fields down to 4.2 K, the hyperfine fields cannot be unequivocally interpreted in terms of either of these factors alone. Line widths were rather high, but noticeably different (0.72 and $0.95 \text{ mm} \cdot \text{s}^{-1}$, respectively, for the outer lines of 38/33 and 3/30).

At 78 K, 38/33 and 3/30 showed markedly different Mössbauer spectra (Fig. 4). Sample 38/33 had broad resonant lines that indicate slow superparamagnetic relaxation, but no collapsed component. Sample 3/30, in contrast, still had a central doublet that made up about 30% of the total spectral area. Sample 38/33, however, had a lower hyperfine field (41.3 T) than that portion of 3/30 that was magnetically ordered (43.5 T). The hyperfine field of sample 3/30 agrees very well with a value of 44.0 T found by Goodman and Lewis (1981) for a similar sample at 77 K.

Mössbauer spectra taken in an intermediate temperature range between 20 and 180 K further emphasize differences in the character of magnetic ordering between

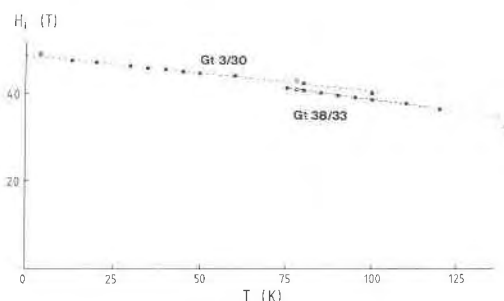


Fig. 6. Hyperfine fields derived from one-sextet fits to magnetically ordered components of goethites 3/30 and 38/33 between 4.2 and 140 K. Open symbols indicate measurements carried out in a bath cryostat.

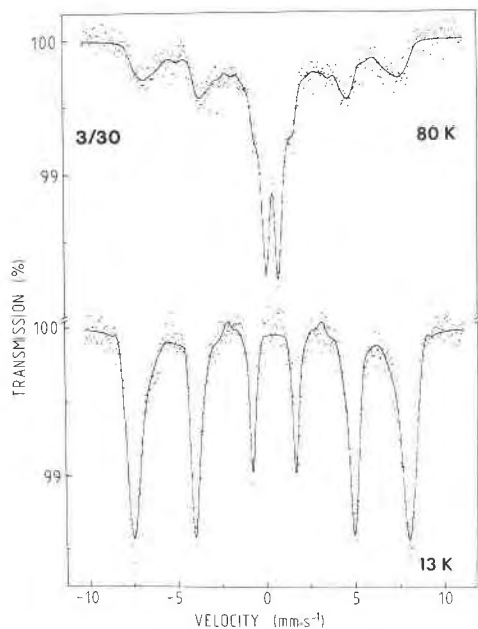


Fig. 7. Mössbauer spectra of goethite 3/30 at 80 and 13 K fitted with distributions of magnetic hyperfine fields.

the two goethites. Sample 38/33 first shows a paramagnetic component at 76 K, whereas for 3/30 a doublet is developed from 29 K onward. The relative areas of the doublets increase approximately linearly with similar slopes as temperatures increase (Fig. 5), and the doublet components make up 50% of the areas under the Mössbauer spectra at about 165 and 110 K for samples 38/33 and 3/30, respectively. Those portions of the spectra that are magnetically ordered, however, show reasonably sim-

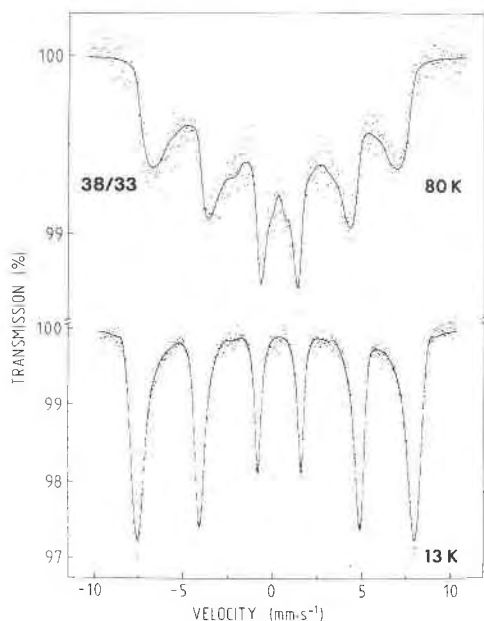


Fig. 8. Mössbauer spectra of goethite 38/33 at 80 and 13 K fitted with distributions of magnetic hyperfine fields.

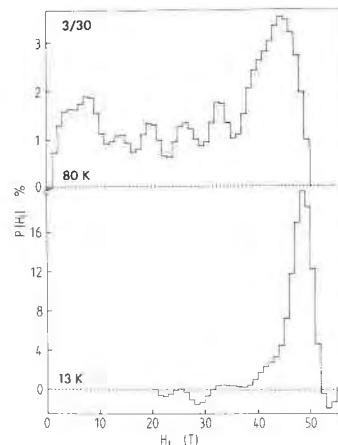


Fig. 9. Distributions of magnetic hyperfine fields in goethite 3/30 at 80 and 13 K.

ilar trends of hyperfine fields (for one-sextet fits) with temperature (Fig. 6).

The fact that—often asymmetrically—widened resonant lines are observed, especially for spectra taken at higher temperatures, indicates the existence of not just *one* discrete hyperfine field (as one-sextet fits would imply) in the magnetically ordered state, but rather distributions of magnetic hyperfine fields (Wivel and Mørup, 1980; Murad, 1982). This is supported by the observation that outer lines were considerably wider than the inner ones down to 4.2 K. Fitting hyperfine-field distributions to the 13 and 80 K spectra (Figs. 7, 8) results in a significantly better delineation of the data than if one-sextet fits are used. With increasing temperatures, these distributions generally become broader, and the fields of maximum probability are shifted to lower values (Figs. 9, 10).

By analogy to spectra of magnetically ordered goethite taken between room temperature and about 120 K, these distributions can be characterized by the fields of maximum probability and the half-widths to the left and right

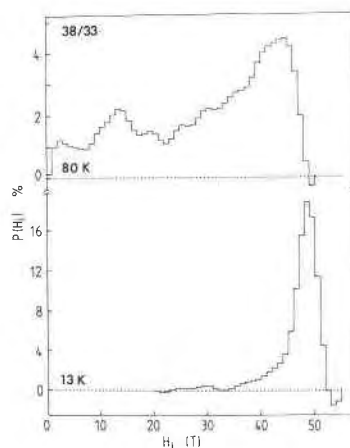


Fig. 10. Distributions of magnetic hyperfine fields in goethite 38/33 at 80 and 13 K.

Table 1. Hyperfine field distribution parameters of magnetically ordered portions of aluminous goethites 38/33 and 3/30 at 13 and 80 K

Temperature	Sample	H_{\max}	HW_1	HW_2
13 K	38/33	48.2	2.1	2.4
	3/30	48.1	2.1	2.5
80 K	38/33	43.6	11.6	3.2
	3/30*	44.1	6.8	3.9

Note: H_{\max} = hyperfine field of maximum probability (T). HW_1 = half-width of hyperfine field distribution below H_{\max} . HW_2 = half-width of hyperfine field distribution above H_{\max} . * Spectrum also contains a doublet with a distribution of quadrupole splittings.

of this maximum (Murad, 1982). For samples 38/33 and 3/30, these coefficients show no significant differences at 13 K. At 80 K, both samples have hyperfine-field distributions that are strongly skewed toward lower fields (Table 1). The smaller magnetically ordered portion of 3/30 at 80 K results in greater scatter for its probability distribution (Fig. 9), but both samples have significant contributions from fields much below the half-widths of the distributions.

DISCUSSION

The quadrupole splitting of sample 38/33, and more so that of 3/30 at room temperature (0.57 and 0.62 $\text{mm} \cdot \text{s}^{-1}$, respectively), is higher than that usually observed for paramagnetic goethite (ca. 0.52 $\text{mm} \cdot \text{s}^{-1}$). In agreement with the small particle size revealed by X-ray diffraction-line broadening and high surface area, this indicates a higher site distortion in 3/30 than 38/33.

Knowing the Al substitutions and surface areas or mean crystallite dimensions of samples 38/33 and 3/30, it is possible to predict the magnetic hyperfine fields that these should have at 4.2 K using Equations 7 and 8 modified from Murad and Schwertmann (1983): $H_i = 50.54 - 3.3Al_i - 0.0036S$, and $H_i = 50.65 - 4.2Al_i - 8.7/MCD_{111}$. On the basis of these equations, Al substitution decreases the hyperfine field of 38/33 by 1.15 T and that of 3/30 by 0.96 T, whereas particle-size effects decrease the hyperfine fields of these samples by 0.12 and 1.07 T, respectively, below the maximum of 50.6 T. Sample 38/33 should therefore have a hyperfine field of 49.3 T and 3/30 a field of 48.6 T. These values compare very well with the actually measured fields of 49.2 and 48.9 T at 4.2 K.

The most obvious differences in the magnetic properties of the two goethites studied are the temperature ranges over which paramagnetic and magnetically ordered phases coexist. The magnetic properties of these phases are apparent from their contributions to Mössbauer spectra taken in the corresponding temperature ranges. Two phenomena can be expected to exert a major influence on the magnetic properties of goethite in this context: an effect of high Al substitution and an effect of small crystal size.

The contribution of a doublet component to the Mössbauer spectra of 38/33 increases from 0 to 50% between 76 and 165 K. In well-crystallized substances, magnetic ordering usually takes place within a relatively narrow temperature range (typically within a few percent of the Néel temperature). The fact that magnetic ordering of sample 38/33 takes place over such a wide temperature range thus would indicate a pronounced influence of crystallinity at first sight. Because this sample consists of quite large, compact crystals, superparamagnetic relaxation can, however, be ruled out. The doublet therefore originates from a genuinely paramagnetic constituent, and its persistence over the observed wide temperature range must be an inherent property of Al-rich goethites.

In the two goethites described here (and in numerous other aluminous goethites studied at 4.2 K), no sign of cation ordering (e.g., superstructure lines observable in X-ray diffraction) could be detected. This and the congruent dissolution of aluminous goethite in HCl (Schwertmann, 1984) indicates a disordered distribution of Fe^{3+} and Al^{3+} ions on the octahedral sites of the goethite structure.

The probability that any Fe^{3+} in an aluminous goethite will have an Al^{3+} ion as neighboring cation increases with the degree of Al substitution. In sample 38/33, almost one out of three Fe^{3+} sites is occupied by an Al^{3+} ion. In the absence of cation ordering, this Fe/Al ratio will, however, not be precisely reflected on an atomic scale, i.e., some Fe^{3+} ions will have more Al^{3+} and fewer Fe^{3+} ions as neighbors than the overall average. The substitution of Fe^{3+} by Al^{3+} thus creates a large number of new crystallographic sites with different nearest-neighbor configurations. Such local compositional fluctuations may also extend into clusters comprising up to several unit cells, i.e., it can be expected that some such clusters in a highly Al-substituted goethite will be richer in Al than others. This local variability in composition will be reflected in properties that are sensitive to short-range structural order-disorder phenomena, e.g., magnetic ordering temperatures and magnetic hyperfine fields. The existence of such local heterogeneities is, for example, particularly evident in aluminous hematites where, within certain compositional limits, phases that have and have not passed through a Morin transition can coexist over considerable temperature ranges (DeGrave et al., 1983).

Because the Néel temperature of goethite is lowered by Al substitution, clusters within a crystal that have a high Al substitution may still be paramagnetic at temperatures at which other, less highly Al-substituted clusters are already magnetically ordered. This leads to the development of coexisting paramagnetic and magnetically ordered components over a Néel temperature range resulting from local compositional variations. Mössbauer spectra of such a substance comprise both a doublet and a sextet in this transitional temperature range.

Thermal scanning data of Fleisch et al. (1980) indicate that an aluminous goethite with $Al_i = 0.306$ should have

a minimum absorption for the 14.4-keV ^{57}Fe gamma-ray at about 210 K. This temperature corresponds to the onset of magnetic order, i.e., the temperature at which the paramagnetic doublet *begins* to give way to a sextet, and is therefore not in conflict with our observation of 50% magnetic order for sample 38/33 at 165 K.

A paramagnetic doublet persists to much lower temperatures in sample 3/30 than in 38/33, in spite of the fact that 3/30 is not as highly Al-substituted. The most likely cause for this is the smaller crystal size of 3/30, i.e., in this sample the influence of small crystal size has been superimposed upon that of high Al substitution. As a result of this, the range of temperatures within which 3/30 orders magnetically has been smeared out more broadly than in 38/33, and a partial relaxational breakdown of magnetic order remains in 3/30 down to 29 K.

The observation that the average hyperfine fields of the magnetically ordered portions of 3/30 and 38/33 do not differ significantly up to about 100 K (although 3/30 has a superparamagnetic component from 29 K onward, whereas 38/33 is completely magnetically ordered up to 76 K) seems somewhat surprising at first sight. There are probably two causes for this: (1) in this temperature range (as at 4.2 K), the magnetic hyperfine field is a function of both Al substitution and particle size, i.e., the higher Al substitution of 38/33 is to some extent compensated by the smaller particle size of 3/30, and (2) only those portions of the samples that are well enough crystallized to be magnetically ordered contribute to the magnetic hyperfine-field distributions at any temperature, i.e., the total spectrum of particle sizes (this concerns in particular the most poorly crystallized components of 3/30) does not come to bear until complete magnetic order has been reached (at 29 K in 3/30).

These results are supported by the hyperfine-field distributions: There are no noticeable differences between samples 38/33 and 3/30 at 13 K or at 80 K, even though a significant portion of the 3/30 spectrum (~24%) has collapsed to a doublet at 80 K.

CONCLUSIONS

In pure goethite, Fe^{3+} occupies a single crystallographic site. Substitution of Fe^{3+} by a diamagnetic ion like Al^{3+} reduces magnetic hyperfine-field supertransfer and thereby reduces average magnetic hyperfine fields. If this substitution takes place without ordering of Al^{3+} , it also creates a variety of new nearest-neighbor configurations and thus new Fe sites. This will lead to ranges of Néel temperatures. These changes in magnetic properties can be observed by Mössbauer spectroscopy.

If aluminous goethites are poorly crystallized, effects of superparamagnetism will be superimposed upon the above-mentioned effects of Al substitution and may thus obscure the latter. A distinction of these two effects is rather complex, but Mössbauer spectra taken over a range of low temperatures enable clarification of the relative contributions of these effects.

ACKNOWLEDGMENTS

We are indebted to U. Schwertmann for placing the samples and unpublished data on these at our disposal, to F. E. Wagner for making access to the 4.2 K equipment at the Physik Department of the T. U. München in Garching possible, to H. C. Bartscherer (Freising-Weihenstephan) for taking the electron micrographs, and to D. G. Lewis and U. Schwertmann for helpful reviews of the manuscript. This study has been supported by the Deutsche Forschungsgemeinschaft under Grant Mu 550/2-1 and by the National Science Foundation under Grant EAR-82-18739. E.M. thanks the Chemistry Department at NCSU for providing a Visiting Assistant Professorship during the spring of 1983.

REFERENCES

- Amarasiriwardena, D.D., DeGrave, Eddy, Bowen, L.H., and Weed, S.B. (1986) Quantitative determination of aluminum-substituted goethite-hematite mixtures by Mössbauer spectroscopy. *Clays and Clay Minerals*, 34, 250–256.
- DeGrave, Eddy, and Vandenberghe, R.L. (1986) ^{57}Fe Mössbauer effect study of well-crystallized goethite ($\alpha\text{-FeOOH}$). *Hyperfine Interactions*, 28, 643–646.
- DeGrave, Eddy, Bowen, L.H., and Hedges, S.W. (1982) Mössbauer spectroscopy with a microprocessor: A versatile software package. *Nuclear Instruments and Methods*, 200, 303–310.
- DeGrave, Eddy, Chambaere, Danny, and Bowen, L.H. (1983) Nature of the Morin transition in Al-substituted hematite. *Journal of Magnetism and Magnetic Materials*, 30, 345–354.
- Fleisch, J., Grimm, R., Grübler, J., and Gülich, P. (1980) Determination of the aluminum content of natural and synthetic aluminogothites using Mössbauer spectroscopy. *Journal de Physique*, 41 C1, 169–170.
- Forsyth, J.B., Hedley, I.G., and Johnson, C.E. (1968) The magnetic structure and hyperfine field of goethite ($\alpha\text{-FeOOH}$). *Journal of Physics C*, 1, 179–188.
- Fysh, S.A., and Clark, P.E. (1982) Aluminous goethite—A Mössbauer study. *Physics and Chemistry of Minerals*, 8, 180–187.
- Golden, D.C., Bowen, L.H., Weed, S.B., and Bigham, J.M. (1979) Mössbauer studies of synthetic and soil-occurring aluminum-substituted goethites. *Soil Science Society of America Journal*, 43, 802–808.
- Goodman, B.A., and Lewis, D.G. (1981) Mössbauer spectra of aluminous goethites ($\alpha\text{-FeOOH}$). *Journal of Soil Science*, 32, 351–363.
- Janot, Christian, and Gibert, Huguette. (1970) Les constituants du fer dans certaines bauxites naturelles étudiées par effet Mössbauer. *Bulletin de la Société française de Minéralogie et Cristallographie*, 93, 213–223.
- Mehra, O.P., and Jackson, M.L. (1960) Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals*, 7, 317–327.
- Mørup, Steen, Madsen, M.B., Franck, Jørgen, Villadsen, Jørgen, and Koch, C.J.W. (1983) A new interpretation of Mössbauer spectra of microcrystalline goethite: "Super-ferromagnetism" or "super-spin-glass" behaviour? *Journal of Magnetism and Magnetic Materials*, 40, 163–174.
- Murad, Enver. (1982) The characterization of goethite by Mössbauer spectroscopy. *American Mineralogist*, 67, 1007–1011.
- Murad, Enver, and Schwertmann, Udo. (1983) The influence of aluminium substitution and crystallinity on the Mössbauer spectrum of goethite. *Clay Minerals*, 18, 301–312.
- Schroerer, Dietrich. (1970) The Mössbauer effect in microcrystals. *Mössbauer Effect Methodology*, 5, 141–162.
- Schwertmann, Udo. (1964) Differenzierung der Eisenoxide des Bodens durch photochemische Extraktion mit saurer Ammoniumoxalat-Lösung. *Zeitschrift für Pflanzenernährung, Düngung und Bodenkunde*, 105, 194–202.

- (1984) The influence of aluminium on iron oxides: IX. Dissolution of Al-goethites in 6 *M* HCl. *Clay Minerals*, 19, 9–19.
- (1985) The effect of pedogenic environments on iron oxide minerals. *Advances in Soil Science*, 1, 171–200.
- van der Woude, F., and Dekker, A.J. (1966) Mössbauer effect in α -FeOOH. *Physica Status Solidi*, 13, 181–193.
- Wivel, Carsten, and Mørup, Steen. (1980) Improved computational procedure for evaluation of overlapping hyperfine field distributions in Mössbauer spectra. *Journal of Physics E*, 14, 605–610.

MANUSCRIPT RECEIVED NOVEMBER 25, 1985

MANUSCRIPT ACCEPTED SEPTEMBER 2, 1986