INFLUENCE OF Al SUBSTITUTION AND CRYSTAL SIZE ON THE ROOM-TEMPERATURE MÖSSBAUER SPECTRUM OF HEMATITE

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Abstract—Mössbauer spectra of 15 hematites with Al substitutions between 0 and 10 mole % were taken at room temperature. X-ray powder diffraction indicated dimensions of these hematites in the *c*-direction to range upwards from 27 nm to crystals large enough to show no line broadening. The Mössbauer spectra showed that magnetic hyperfine fields decreased both with increasing Al-for-Fe substitution and with decreasing crystal size. These relationships indicate that hyperfine field variations cannot, as has been done in the past, be unequivocally related to Al substitution alone. Hyperfine field reductions were paralleled by Mössbauer line broadening due to hyperfine field distributions. Only the hematites heated to 1000°C showed a significant variation of quadrupole splittings with Al substitution. No dependence of quadrupole splitting on crystal size was observed, indicating no detectable distortion of coordination polyhedra in the particle size range studied.

Key Words—Aluminum, Hematite, Iron, Mössbauer spectroscopy, Particle size.

INTRODUCTION

In the course of the past decade, recognition of the possibilities offered by Mössbauer spectroscopy for the characterization of iron oxides in complex natural systems, such as soils, sediments, and mine spoils, has led to increasing applications of this method. Mössbauer spectroscopy permits, from information on the magnetic hyperfine field (H_i) and quadrupole splitting (ΔE_Q), the identification of iron oxides in concentrations as small as about 0.1%. These phases can, in addition, be characterized with respect to their crystallinities and/or ionic substitutions of other elements for iron.

A necessary prerequisite for the successful application of Mössbauer spectroscopy for this purpose is that the iron oxide(s) to be studied must be magnetically ordered. Of all the oxides of trivalent iron, hematite (α-Fe_2O_3) has both the highest temperature below which it is magnetically ordered ($T_C = 955$ K) and the highest saturation hyperfine field ($H(0) = 54.2$ T). At room temperature the reduced temperature (T/T_C) is 0.31, and $H_i/H(0) = 0.97$ in the absence of particle size effects.

Natural hematites may order at less than 955 K because of small particle size (due to superparamagnetic relaxation) or substitution of other elements (in particular Al) for Fe. Hematites <8 nm in size are superparamagnetic at room temperature (Janot *et al.*, 1973). Measurements on such samples must therefore be carried out at lower temperatures to attain magnetic order.

In practice, both natural and synthetic hematites tend to have particle size distributions rather than a single, well-defined particle size. Components of such samples with particle sizes >8 nm should therefore be magnetically ordered at room temperature.

An additional complication arises from the fact that pure, well-crystallized hematite has a magnetic transition at about 260 K (Morin, 1950). Between its magnetic ordering temperature and this "Morin transition" hematite is weakly ferromagnetic; below the Morin transition it is antiferromagnetic. As temperatures decrease from above to below the Morin transition, the magnetic hyperfine field of hematite drops by about 0.7 T and the quadrupole splitting changes sign and increases about twofold.

Both poor crystallinity and substitution of Fe by Al lower the Morin temperature. Kündig *et al.* (1966) observed no Morin transition for hematites with an average particle diameter of 18 nm at temperatures as low as 10 K; similarly Krén *et al.* (1974) observed no Morin transition at an Al-for-Fe substitution of 9 mole %. In an intermediate crystallinity or substitution range two spectra can be observed at low temperatures: one each for hematite which has or has not passed through a Morin transition (Nininger and Schroeer, 1978; DeGrave *et al.*, 1982).

Ibanga *et al.* (1983) and Schwertmann and Kämpf (1985) showed that soil hematites commonly have average particle sizes >8 nm. Room-temperature spectra of such components can thus be used for the identification of hematite and its distinction from other iron oxides without sophisticated cryogenic equipment and expensive coolants. Furthermore, hematite is always above the Morin transition at room temperature, so that Mössbauer spectra of magnetically ordered hematite show one magnetic component only.

The substitution of Fe by Al reduces the magnetic hyperfine field of hematite at all temperatures (Janot and Gibert, 1970). Fysh and Clark (1982) observed

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different interrelations between the magnetic hyperfine fields of aluminous hematites synthesized by calcination of aluminous goethites at 950° and 590°C, respectively, and attributed these differences to a "c-axis disorder" (with respect to which they did not, however, characterize their samples). In a recent review, Bowen and Weed (1984) listed several different published relationships between the magnetic hyperfine field of hematite at room temperature and the degree of Al substitution. These relationships, for example, show distinctive discrepancies in the hyperfine fields for Al-free hematites, which vary between 50.9 T (Jónás *et al.,* 1980) and 51.79 T (Fysh and Clark, 1982). Although part of this variation may result from differences in measuring techniques (e.g., use of a laser interferometer or different standards for velocity calibration), it does suggest that an evaluation not merely of the influence of Al substitution, but of the simultaneous effects of Al substitution *and* crystallinity is called for.

In the present study, room-temperature Mössbauer spectra of synthetic hematites of different Al substitutions and crystal sizes are described. Such spectra can give information on the presence of hematite in mineralogically complex samples, on the crystallinity of such hematites, and on the extent of Al substitution. It is our intention to emphasize the influence of Al substitution *and* crystal size on the magnetic properties of hematite at room temperature and thus provide a basis for a more realistic characterization of this mineral in natural systems than if only Al substitution is taken into consideration.

MATERIALS AND METHODS

One series of hematites with different Al contents (series 17; original samples of Schwertmann *et al.,* 1979) was prepared by storing aluminous ferrihydrites under water at pH 7 and 70°C for 77 days. The Al contents of the hematites formed were determined chemically. X-ray powder diffraction line broadening indicated mean crystal diameters parallel to [001] (MCD_c) between 27 and 40 nm (Schwertmann *et al.,* 1979).

A second suite of hematites that showed no effects of crystallinity ("bulk" samples) was prepared by direct calcination of aluminous ferrihydrites and hematites of the aforementioned series 17 for 48 hr at 1000°C (series 14/1000 and 17/1000, respectively). These samples are identical to those for which 4.2-K spectra were described by Murad (1984). Al contents of the hematites were determined chemically after removal of free Al oxides with 5 N NaOH at 70°C.

Mössbauer spectra were obtained using a $^{57}Co/Rh$ source moved in a sinusoidal mode. Two sets of absorbers were prepared: one consisted of a 1:1 mixture of hematite with sugar; the other consisted of a 2:1:3 mixture of hematite : Fe powder (Merck Analytical Reagent #3819) : sugar. Mixtures giving hematite concen-
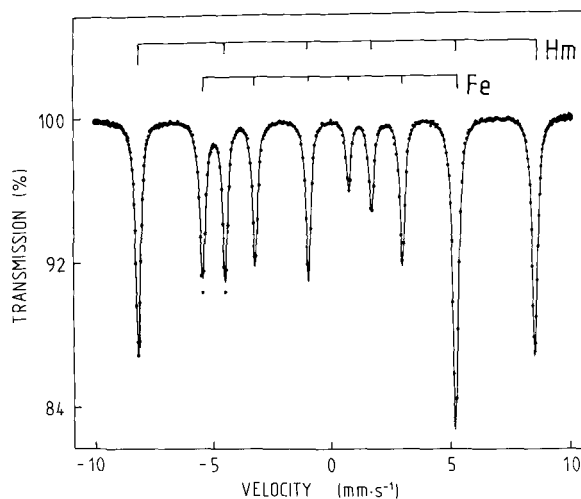

Figure 1. Mössbauer spectrum of sample 14/0-1000 taken together with a 6-μm iron foil at 294 K. Individual spectral components are indicated with bar diagrams.

trations of about 9 mg Fe/cm² were placed in a Plexiglas holder; the first set of samples was measured with a 6-μm thick Fe foil taped to the sample holder. Measurements were carried out at 294 ± 1 K. The magnetic hyperfine field for the iron foil, recalculated from the data of Violet and Pipkorn (1971) using a Brillouin function, was taken as 33.07 T. Parameters were averaged from the two measurements. Data from the latter measurements were also used to determine the variation of recoil-free fractions (Murad, 1985).

The transmitted radiation was recorded with a Kr-filled proportional counter, and the data were stored in a 1024 channel analyzer. After sufficiently good statistics had been attained, the mirror halves of the spectrum were folded and Lorentzian line fits were carried out using a CDC Cyber 175 computer. Corresponding lines of each sextet were constrained to have equal widths and intensities.

Magnetic hyperfine fields (H_i), quadrupole splittings (ΔE_Q), and half widths of lines 1 and 6 (WID_1), lines 2 and 5 (WID_2), and lines 3 and 4 (WID_3) of the Mössbauer spectra were used to characterize the hematites studied. Correlation of these parameters with the degree of Al substitution ($Al_s = Al/(Al + Fe)$) and mean crystal sizes and other statistical calculations were carried out using SPSS version 9 on the same computer system. Individual values are listed in Table 1.

RESULTS

A typical spectrum, obtained for the Al-free sample of series 14/1000 run together with the Fe foil at 294 K, is shown in Figure 1. Because some peaks of the Fe foil and hematite overlap, a bar diagram showing the positions of the individual lines and their relative intensities is included.

Table 1. Mössbauer data for Al-substituted hematites at room temperature.

Sample[1]	Chemical/XRD Data		Mössbauer data[3]				
	Al/(Al + Fe)	MCD_c[2]	WID_1	WID_2	WID_3	ΔE_Q	H_i
14/0-1000	0.000	bulk	0.269	0.273	0.258	−0.187	51.77
17/2-1000	0.018	bulk	0.285	0.276	0.267	−0.197	51.60
17/4-1000	0.043	bulk	0.302	0.283	0.265	−0.201	51.48
14/5-1000	0.049	bulk	0.314	0.296	0.267	−0.200	51.38
17/6-1000	0.053	bulk	0.326	0.306	0.262	−0.203	51.33
17/8-1000	0.072	bulk	0.341	0.315	0.264	−0.205	51.20
17/10-1000	0.095	bulk	0.374	0.326	0.273	−0.214	50.94
14/10-1000	0.098	bulk	0.369	0.325	0.278	−0.209	51.00
17/0-70	0.000	40	0.359	0.347	0.319	−0.204	51.02
17/1-70	0.008	53	0.359	0.342	0.288	−0.205	50.97
17/2-70	0.018	77	0.354	0.326	0.277	−0.204	50.96
17/4-70	0.043	55	0.377	0.347	0.288	−0.205	50.95
17/6-70	0.053	67	0.434	0.387	0.294	−0.207	50.65
17/8-70	0.072	51	0.483	0.427	0.330	−0.200	50.33
17/10-70	0.095	27	0.570	0.500	0.353	−0.203	49.92

[1] /n−x = n indicates percent mole ratio Al/(Fe + Al) in the synthesis solution; x (1000 or 70) indicates synthesis temperature in °C.

[2] MCD_c = mean crystal diameters parallel [001] as determined by X-ray powder diffraction (XRD); bulk indicates no appreciable line broadening.

[3] Mössbauer line widths (WID_1, WID_2, WID_3) and quadrupole splitting (ΔE_Q) given in mm/s; magnetic hyperfine fields (H_i) given in T.

The inter-spectral variation of parameters (i.e., statistical plus instrumental errors) is indicated by the variation of parameters observed for the iron components. Average values and errors on the last digit (in parentheses) of the isomer shift relative to the ^{57}Co/Rh source and quadrupole splitting for Fe components in the 30 spectra recorded in the course of this study are −0.113(2) and +0.007(3) mm, respectively, with no significant differences between the Fe foil and powder. Line widths for the Fe foil averaged 0.258(9), 0.257(8), and 0.25(2), and for the Fe powder 0.271(8), 0.271(7), and 0.273(8) mm/s from the outer to the inner line pairs, respectively.

For the eight bulk (i.e., heated to 1000°C) hematites, H_i, WID_1, WID_2, and ΔE_Q showed linear dependences on Al_s that were significant at the 0.1% level. A less significant relation was observed for the dependence of WID_3 on Al_s. The numerical relationships are given by:

$$H_i(T) = 51.78 - 8.2(Al_s) \qquad r = -.993,$$
$$WID_1 \text{ (mm/s)} = 0.265 + 1.08(Al_s) \qquad r = .991,$$
$$WID_2 \text{ (mm/s)} = 0.268 + 0.60(Al_s) \qquad r = .967,$$
$$\Delta E_Q \text{ (mm/s)} = -0.190 - 0.22(Al_s) \qquad r = -.956,$$
$$WID_3 \text{ (mm/s)} = 0.259 + 0.14(Al_s) \qquad r = .786.$$

Corresponding significant relations for the seven series 17 hematites are:

$$H_i(T) = 51.15 - 11(Al_s) \qquad r = -.929,$$
$$WID_1 \text{ (mm/s)} = 0.33 + 2.2(Al_s) \qquad r = .939,$$
$$WID_2 \text{ (mm/s)} = 0.32 + 1.6(Al_s) \qquad r = .900,$$

i.e., the correlations are less pronounced for the 70°C hematites than for the bulk hematites. The data for the

series 17 hematites furthermore show systematic deviations from linear trends with a maximum at an Al substitution of about 4 mole %, paralleling variations in crystal size within this series (Schwertmann *et al.*, 1979). No significant correlations between the widths of the inner lines (r = .63) or the quadrupole splitting (r = .36) and Al_s were observed for the series 17 hematites.

The differences in slopes of the H_i, WID_1, and WID_2 vs. Al_s relations of the bulk and series 17 hematites given by the above equations are statistically significant and may result from an overall decrease in crystal size with Al substitution within the series 17 samples. Above
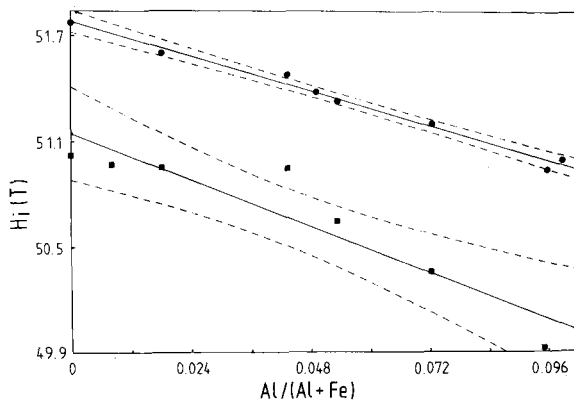

Figure 2. Variation of magnetic hyperfine fields of hematites formed at 70°C (squares) and 1000°C (circles) at room temperature as a function of Al substitution. Regression lines for the two samples series are bordered with 95% confidence intervals.
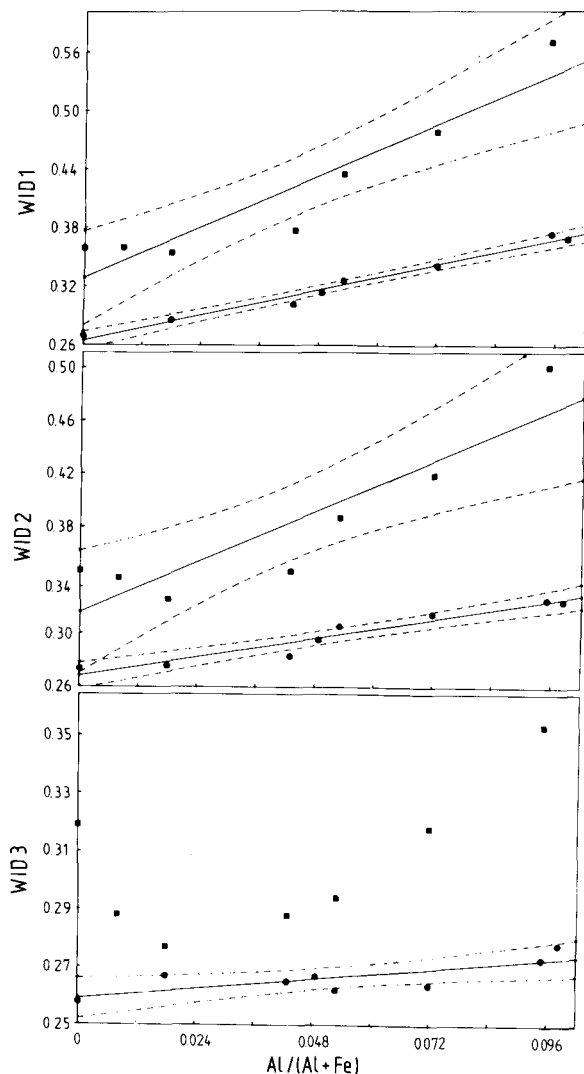
Figure 3. Variation of widths of outer (WID$_1$), second and fifth (WID$_2$), and inner (WID$_3$) lines of room-temperature Mössbauer spectra of hematites formed at 70°C (squares) and 1000°C (circles) as a function of Al substitution.
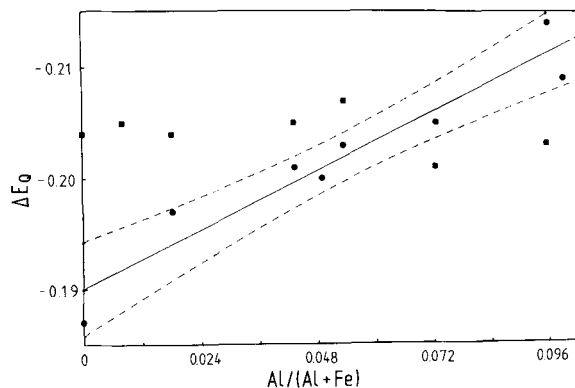

Figure 4. Variation of the quadrupole splitting of room-temperature Mössbauer spectra of hematites formed at 70°C (squares) and 1000°C (circles) as a function of Al substitution.

lation coefficients for H$_i$ (−.53), WID$_1$ (.56), WID$_2$ (.45), and WID$_3$ (.23) vs. Al$_s$. Multiple linear regression analyses of H$_i$ and line widths as dependent variables vs. Al$_s$ and MCD$_c$ as independent variables, however, produce the following, considerably improved equations for all 15 samples:

$$H_i(T) = 51.72 - 7.6(Al_s) - 32/MCD_c$$
$$r = .971,$$
$$WID_1 \ (mm/s) = 0.254 + 1.3(Al_s) + 5.2/MCD_c$$
$$r = .976,$$
$$WID_2 \ (mm/s) = 0.256 + 0.8(Al_s) + 4.3/MCD_c$$
$$r = .976,$$
$$WID_3 \ (mm/s) = 0.255 + 0.19(Al_s) + 2.1/MCD_c$$
$$r = .966.$$

The quadrupole splitting was observed to vary with Al$_s$, and Al$_s$ plus MCD$_c$, respectively, as follows:

$$\Delta E_Q \ (mm/s) = -0.198 - 0.10(Al_s) \qquad r = -.574,$$
$$\Delta E_Q \ (mm/s) = -0.197 - 0.10(Al_s) - 0.07/MCD_c$$
$$r = .592,$$

i.e., only a subordinate correlation exists between ΔE_Q and Al$_s$, which is just slightly improved by taking crystal size into consideration.

At room temperature the magnetic hyperfine field and Mössbauer line widths of hematite thus depend not only on the substitution of Fe^{3+} by Al^{3+}, but also on crystal size. The quadrupole splitting, on the other hand, was observed to vary systematically with Al$_s$ only for the bulk hematites and showed no relation to crystal size.

DISCUSSION

Published relations between the Al substitution and the magnetic hyperfine field of hematite at room temperature essentially lie within the range of those given

Al/(Al + Fe) ratios of about 0.1, the data deviate markedly from linearity, so that linear fits are no longer justified (DeGrave *et al.,* 1982).

The variations of the named parameters with Al substitution for the two studied series are shown in Figures 2–4. For each significant relation, linear regression lines are plotted together with 95% confidence intervals for the corresponding regression. The differences in trends observed for the two series are statistically significant where the confidence intervals do not overlap.

Simple linear regression analysis of the Mössbauer data vs. Al substitutions of *both* the bulk and series 17 hematites together gives not very satisfactory corre-

above for the series 17 and bulk hematites. The dependence of the magnetic hyperfine field of hematite on crystal size alone as determined by electron microscopy was studied by Tsuji *et al.* (1984), who noted significant reductions in magnetic hyperfine fields as crystals became smaller than 1.5 μm.

The mechanisms causing the variations in magnetic hyperfine fields are conceivably related: by reducing crystal sizes, an increasing number of Fe^{3+} ions come to lie near particle surfaces or next to defects. The correspondingly lower number of Fe^{3+} neighbors causes a reduction of the supertransferred hyperfine field, just as does the substitution of a diamagnetic ion (e.g., Al^{3+}) for Fe^{3+}. An alternative explanation for the reduction in hyperfine fields with particle size is that the collective direction of magnetization may fluctuate somewhat in very small particles (Mørup, 1983).

It follows that if Al substitutions of hematites are to be determined from the magnetic hyperfine fields at room temperature, it is necessary to have knowledge of their crystal size, otherwise too high values of Al substitution may be deduced. On the basis of the above arguments and analogous to measurements on goethites (Murad and Schwertmann, 1983), such an influence can also be expected at lower temperatures (at which, however, the influence of *both* Al substitution and crystal size on the hyperfine field will be reduced somewhat and therefore not be as obvious as for room-temperature measurements). The observed dependence of the quadrupole splitting on Al substitution (for the bulk hematites) but not on crystal size indicates that the coordination polyhedra are not noticeably distorted as crystals become smaller in the particle-size range studied.

The widths of the outer lines of the Mössbauer spectra increase systematically both with increasing Al substitution and decreasing crystal size. The ratio of the Al_s and MCD_c coefficients in the equations relating the widths of the outer lines to these variables is almost identical to that in the equation relating H_i to the same variables; thus, these equations cannot be solved to determine Al_s *and* MCD_c. The influence of Al substitution and crystal size on line widths tapers off from the outer to the inner lines. The increasing line widths are therefore due to distributions of hyperfine fields and not due to distributions of quadrupole splittings (which would affect all lines to an equal extent). These distributions of hyperfine fields result from local variations in the environments of the resonant atoms, i.e., next-nearest neighbor effects, and confirm the similar influence of Al substitution and decreasing crystal size on the magnetic properties of hematite.

The divergence from linearity observed for the parameters of the series 17 hematites (but not for the bulk hematites) parallels a maximum crystal size within the series 17 samples (Schwertmann *et al.,* 1979) and related variations of the recoil-free fraction (DeGrave *et*

al., 1985; Murad, 1985). It therefore supports the conclusion that both crystallinity and Al substitution affect the Mössbauer parameters in a similar manner.

ACKNOWLEDGMENTS

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