

# QUANTITATIVE DETERMINATION OF ALUMINUM-SUBSTITUTED GOETHITE-HEMATITE MIXTURES BY MÖSSBAUER SPECTROSCOPY

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**Abstract**—Mixtures of synthetic Al-substituted goethite ( $\alpha\text{-Fe}_{0.814}\text{Al}_{0.186}\text{OOH}$ ) and hematite ( $\alpha\text{-Fe}_{1.658}\text{Al}_{0.342}\text{O}_3$ ) (75, 50, 25, 3% hematite by weight) were studied by Mössbauer spectroscopy to evaluate the use of that technique for quantitative analysis. Mössbauer spectra for these mixtures, obtained in the temperature range 12–130 K, were better fitted by a distribution of magnetic fields than by two magnetic sextets. Spectra at 80 K were equally as good as those from lower temperature to determine the hematite-goethite ratio. The recoil-free fractions of the individual components were about equal at any fixed temperature, but thickness effects caused as much as 30% error in the determination of the ratio of components in mixtures.

**Key Words**—Aluminum, Goethite, Hematite, Mössbauer spectroscopy, Quantitative mineralogy.

## INTRODUCTION

Mössbauer spectroscopy is becoming increasingly important as a technique for the study of iron-containing minerals in soils and clays because of its specificity for iron and its ability to distinguish various iron minerals (Goodman, 1980), in particular goethite ( $\alpha\text{-FeOOH}$ ) and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ). Pure hematite (Kundig *et al.*, 1966) and pure goethite (Forsyth *et al.*, 1968) are both magnetically ordered at room temperature (RT) and below. Because they possess distinctly different hyperfine fields, they may be easily distinguished by their Mössbauer spectra. In soils both minerals commonly contain varying amounts of Al replacing Fe (Norrish and Taylor, 1961; Schwertmann *et al.*, 1977; Bigham *et al.*, 1978). Al reduces the observed hyperfine field in both goethite (Golden *et al.*, 1979; Fysh and Clark, 1982a; Murad and Schwertmann, 1983) and hematite (DeGrave *et al.*, 1982a; Fysh and Clark, 1982b), and the reduction may be used to estimate Al substitution in these minerals. Spectra at low temperature ( $\leq 80$  K) are required to obtain Al content in goethite by this method, because RT spectra of aluminous goethite are identical to those of many silicate minerals containing  $\text{Fe}^{3+}$ .

A number of papers have reported the use of Mössbauer spectroscopy to estimate relative proportions of goethite and hematite in soils and soil clays (e.g., Ko-

dama *et al.*, 1977; Bigham *et al.*, 1978; Golden *et al.*, 1979; Childs *et al.*, 1979; Bowen and Weed, 1981; Schwertmann *et al.*, 1982; Ibanga *et al.*, 1983). The relationship between measured absorption peak area,  $A_i$ , in the Mössbauer spectrum and iron content,  $n_i$ , (atom or wt. % Fe) is linear for a thin absorber, but depends on the recoil-free (Mössbauer) fraction,  $f_i$ , of that species. Thus, for a mixture of goethite and hematite:

$$A_g/A_h = f_g n_g / f_h n_h \quad (1)$$

where the ratio  $\epsilon = f_g/f_h$  is required for quantitative analysis. Several of the above mentioned authors used synthetic mixtures to determine this ratio at 4 K (Bigham *et al.*, 1978; Schwertmann *et al.*, 1982), and absolute values of  $f_g$  and  $f_h$  were reported by Fysh and Clark (1982a, 1982b) as a function of Al substitution. The values of both  $f_g$  and  $f_h$  increased with Al content ( $f_g = 0.69$  for 0% Al, 0.89 for 18.7% Al), but were about the same for a given substitution. Fysh and Clark (1984) discussed the use of pseudo-Lorentzian lines to analyze Mössbauer spectra of goethite-hematite mixtures in bauxite.

In contrast to the above studies at 4 K, little information is available for  $\epsilon$  between 4 and 300 K, although liquid nitrogen temperature (77 K) is much simpler and cheaper to maintain than 4 K for routine Mössbauer spectroscopy. In the present paper Mössbauer results on mixtures of synthetic aluminous goethite and hematite are presented for spectra over a range of temperature from  $\sim 12$  to 130 K. Quantitative ratios of the two components and most parameters of mineralogical

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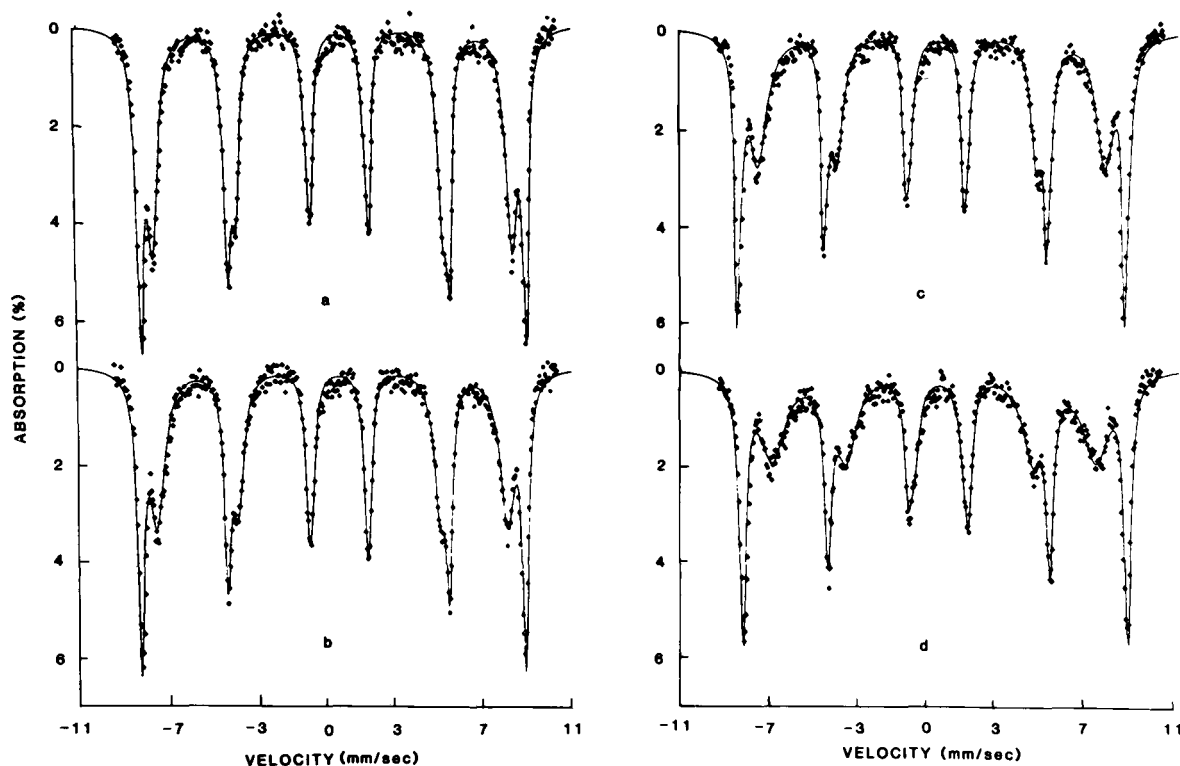


Figure 1. Mössbauer spectra of 50-50 goethite-hematite mixture as function of temperature, fitted with two sextets. (a) 15 K, (b) 60 K, (c) 80 K, (d) 130 K.

interest were obtained equally well from 80 K spectra as from those obtained at lower temperature by use of a spectral fitting procedure which assumed broad distribution of magnetic fields for both components.

## EXPERIMENTAL

### Samples

Al-substituted goethites,  $\text{Fe}_{0.814}\text{Al}_{0.186}\text{OOH}$  and  $\text{Fe}_{0.829}\text{Al}_{0.171}\text{OOH}$ , were prepared using hydrothermal synthesis (Golden, 1978). The latter product was converted to hematite by heating at 500°C (DeGrave *et al.*, 1982a). The Fe and Al were determined in the goethites by atomic absorption spectroscopy after dissolving suitable samples in an HCl solution. Mixtures of 75, 50, 25, and 3% by weight of the hematite (17.1 mole % Al) and goethite (18.6 mole % Al) were analyzed by Mössbauer spectroscopy. Absorbers contained 10-20 mg Fe/cm<sup>2</sup> and were mixed with powdered sugar to obtain a uniform sample distribution. Absorbers of the pure components were also analyzed. Sample thicknesses of 2-10 mg Fe/cm<sup>2</sup> were analyzed.

### Mössbauer spectra

Mössbauer spectra were obtained as a function of temperature from ~12 to 295 K using a closed-cycle cryostat for cooling the absorber (maintained to within ~0.1 K). The source (~50 mCi <sup>57</sup>Co/Rh) was at room

temperature. Velocity calibration was by laser interferometry. The experimental system has been previously described (DeGrave *et al.*, 1982b).

### Data analysis

The spectra were fitted, after subtraction of the small peaks due to Fe in the spectrometer windows, to either a combination of two magnetic sextets, one each for goethite and hematite, or to two distributions of sextets. For both procedures the line shape was assumed to be Lorentzian, although the spectra of the pure components were also fitted with pseudo-Lorentzian sextets, as suggested by Fysh and Clark (1984).

In the two sextet fits, the quadrupole interaction  $\Delta$  ( $\Delta = \frac{1}{4}e^2qQ[3 \cos^2 \theta - 1]$ , where  $q$  is the principal component of the electric field gradient,  $Q$  is the nuclear quadrupole moment,  $e$  is the electron charge, and  $\theta$  is the angle between magnetic and electric field gradient axes) and the hyperfine field  $H$  were independent variables for each sextet, as were line intensities and line widths. The narrow hematite lines were, however, assumed to have equal width, and the innermost peaks of the hematite sextet, which overlap with goethite, were generally assumed to have  $\frac{1}{3}$  the intensity of the outermost peaks of the sextet. The isomer shifts  $\delta$  of goethite and hematite were identical within experimental error, but a small difference in quadrupole in-

Table 1. Mössbauer parameters for 50–50 weight percent goethite-hematite mixture.<sup>1</sup>

T (K)	Two sextets			H (kOe)	Field distribution			LHW <sup>2</sup> (kOe)
	$\delta$ (mm/s)	$\Delta$ (mm/s)	$\Gamma$ (mm/s)		$\delta$ (mm/s)	$\Delta$ (mm/s)	$H_{max}$ (kOe)	
15 G	0.36	-0.27	0.61	494	0.37	-0.26	495	13
H	0.36	-0.21	0.34	530	0.37	-0.21	530	9
20 G	0.36	-0.26	0.58	493	0.37	-0.24	493	13
H	0.36	-0.20	0.36	529	0.36	-0.21	529	11
60 G	0.36	-0.27	0.84	481	0.36	-0.26	484	16
H	0.36	-0.21	0.33	528	0.36	-0.21	528	11
80 G	0.35	-0.26	0.94	471	0.36	-0.26	476	22
H	0.36	-0.21	0.34	527	0.36	-0.21	527	11
110 G	0.34	-0.27	1.2	454	0.35	-0.26	464	34
H	0.35	-0.21	0.34	525	0.35	-0.21	524	11
130 G	0.35	-0.28	1.4	440	0.36	-0.20	453	38
H	0.34	-0.21	0.58	523	0.34	-0.21	522	11

<sup>1</sup> For the two sextet fits,  $\Gamma$  is the peak width at half-maximum for the outmost goethite lines and for all lines of the hematite sextet,  $\delta$  is isomer shift relative to Co(Rh) at room temperature,  $\Delta$  is quadrupole interaction. For the field distributions, the magnetic field range was 310–510 kOe for goethite, 510–540 for hematite in steps of 5 kOe except for T  $\geq$  80 K where the range was 310–500, 500–540 kOe.

<sup>2</sup> LHW is half width of the field distribution on the lower field side.

teraction was noted:  $\Delta = -0.21$  mm/s for hematite and  $-0.27$  mm/s for goethite, in agreement with literature data (Golden *et al.*, 1979; DeGrave *et al.*, 1982a).

The field distribution method of Wivel and Mørup (1981) was used as an alternative method of spectral analysis. Several changes were made in the original program, based in part on a version supplied by R. Vandenberghe (Laboratory for Magnetism, Proeftuinstraat 86, B-9000 Gent, Belgium) and in part on our own requirements using an IBM 3081 Computer at the Triangle Universities Computing Center (TUCC). The revised program was also based on the fast iteration subroutine of the IMSL Inc. library, ZXSSQ, using the Levenberg-Marquardt algorithm. Our revised program fit several distributions of either magnetic hyperfine field or quadrupole splitting (the latter was not used in the present work). Least squares adjustable parameters were the baseline counts and the isomer shift  $\delta$  and quadrupole interaction  $\Delta$  for each field distribution. The intensity ratios were fixed at the theoretical ratios: 3.0:2.0:1.0 for both hematite and goethite. These ratios could have been made adjustable parameters, but the increase in computer time did not seem justified. A distribution for quadrupole interaction,  $\Delta$ , was not needed, because the spectra were symmetric about their midpoint. Variation in  $\Delta$  would produce spectra with different intensities for the positive and negative velocity components.

The line widths for each sextet of a distribution were fixed equal, and certain smoothing parameters were specified for each distribution. Trial analyses of the present samples established that the smoothing parameters  $\gamma = 10^{-3}$  and  $\beta = 10$  gave consistent results according to the criteria of Wivel and Mørup (1981),

using third-order smoothing. Line widths were arbitrarily fixed at 0.33 mm/s for goethite and 0.27 mm/s for hematite. A range of hyperfine fields from 310 to 540 kOe was used, in steps of 5 kOe. The dividing cut-

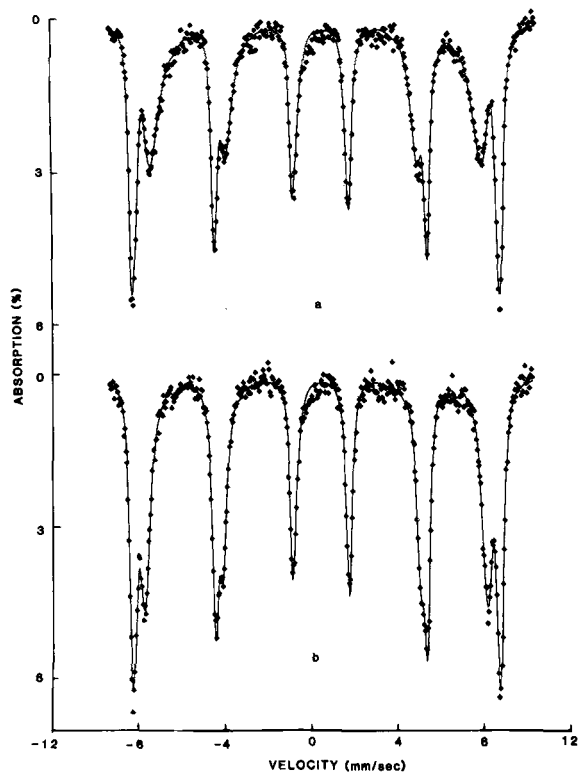


Figure 2. Mössbauer spectra of 50–50 goethite-hematite mixture, fitted with two distributions of hyperfine fields. (a) 80 K, (b) 15 K. See Figure 3 for the distributions.

Table 2. Relative Mössbauer spectral peak areas and  $\chi^2$  from two fitting procedures.<sup>1</sup>

Mixture	T (K)	Two sextet		Field distribution	
		$\chi^2$	R.A.H. (%)	$\chi^2$	R.A.H. (%)
50G-50H	15	703	45	631	47
	20	1247	42	1391	44
	60	763	43	645	49
	80	769	44	623	50
	110	1076	42	858	51
	130	705	42	658	52
25G-75H	13	965	73	969	71
	20	932	71	829	70
	42	1085	73	1076	70
	60	1325	68	1603	70
	80	1307	68	1490	72
	100	1089	69	1002	72
75G-25H	20	728	19	698	25
	40	1025	18	737	25
	60	1633	16	1052	24
	80	1044	14	579	26
	100	1177	25	642	26
97G-3H <sup>2</sup>	12.5	—	—	673	2.2
	20	—	—	625	2.6
	40	—	—	583	2.8
	60	—	—	527	3.3
	80	—	—	587	2.8

<sup>1</sup> The relative peak area for hematite (R.A.H.) is compared to total absorption (hematite + goethite). The field distributions were taken in steps of 5 kOe from 310 to 540 kOe, with the upper limit for goethite at 510 kOe ( $T \leq 60$  K) or 500 kOe ( $T \geq 80$  K). The  $\chi^2$  is for 432 data points and 13 adjustable parameters (two-sextet fits) or 52 parameters including 47 fields with adjustable probability (field distributions).

<sup>2</sup> Two sextets could not be fitted to these spectra.

off between goethite and hematite was fixed at 510 kOe for  $T \leq 60$  K and 500 kOe for  $T \geq 80$  K.

The program iterated the background counts and the isomer shift and quadrupole interaction independently for each distribution. In addition to these parameters it gave a probability for each sextet of each distribution as it contributed to the experimental spectrum. The important feature of this analysis was that it made no prior assumption as to shape of the hyperfine field distribution, which in the present samples was due to Al substitution and, possibly, particle size effects. If only one distribution was assumed for a mixture of goethite and hematite, the hematite was clearly displayed as a separate peak in the distribution at higher magnetic fields. The program required considerable computer time, however; the CPU time using an IBM 3081 computer was less than 5 min only if input guesses for the adjustable parameters were close to the final, iterated values.

## RESULTS AND DISCUSSION

A series of spectra for the 50-50 goethite-hematite mixture is shown in Figure 1. These were fitted with

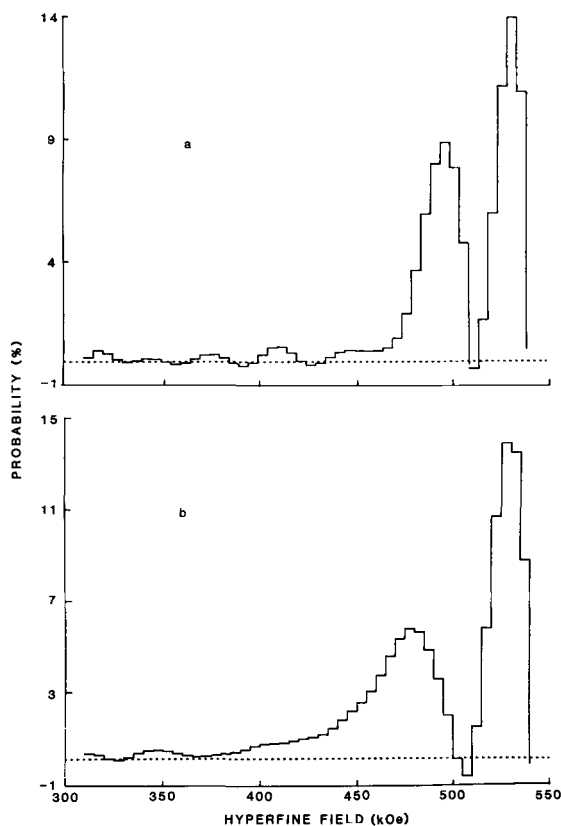


Figure 3. Probability distributions of hyperfine fields for the 50-50 goethite-hematite mixture. (a) 15 K, (b) 80 K.

two sextets. The inner goethite sextet exhibits asymmetric line broadening above about 20 K. The results from the two sextet fits for this mixture are listed in Table 1. The isomer shift  $\delta$  and quadrupole interaction constant  $\Delta$  changed very little with temperature, but the hyperfine field decreased with increased temperature, more for goethite than for hematite. The line width  $\Gamma$  for goethite increased markedly with temperature. Some of these spectra fitted using the field distribution method are shown in Figure 2. The values of  $\delta$  and  $\Delta$  determined from the field distribution were the same as those determined by the two sextet method. The field of maximum probability for goethite,  $H_{\max}$ , decreased with temperature at a lesser rate than  $H$  from the two sextet fit (Table 1). In Table 2 the relative peak areas as determined from the two methods are compared. As seen in Table 2, the relative peak area (R.A.H.) of hematite showed no distinct trend with temperature for either fitting procedure. The  $\chi^2$  for the field distribution was generally lower, but not appreciably so. It should be noted that the field distribution fitting procedure had a smaller number of degrees of freedom than the two sextet fits, because each field contributed one adjustable parameter to the fit. Using 432 data points, however, the variation in degrees of freedom was only about 10% between the two fitting procedures.

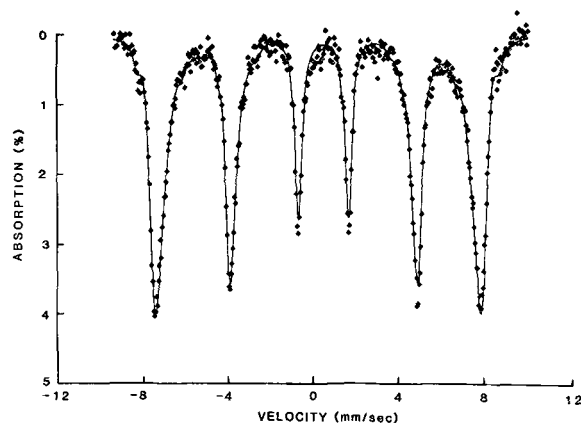


Figure 4. Mössbauer spectrum of 3% hematite in goethite at 80 K fitted with a single distribution of hyperfine fields.

The average R.A.H. was consistently higher for the field distribution (49%) than for the two sextet method (43%). The latter method overestimated the goethite contribution, even at 15 K. For this mixture the proportion of iron in hematite form was actually 53%. Thus, the field distribution gave a result closer to the correct value than the two sextet analysis, but was still low.

To test whether this difference was due to differing recoil-free fractions or to an overestimation of the goethite peak area by the fitting procedure, spectra were obtained for mixtures containing 75, 25, and 3% hematite and for the individual components. The relative area analyses for the mixtures are listed in Table 2. For 75% hematite the two spectral analysis procedures agreed, 70% from the two sextet fits and 71% for the distributions, but these values were lower than the correct value (77%). Using the average R.A.H. for the distributions, a value of  $\epsilon = 1.37$  was calculated (cf.  $\epsilon = 1.17$  for the 50–50 mixture discussed above).

The results for the 25% hematite mixture were more striking. The two sextet analysis gave R.A.H. values which varied inconsistently with temperature (Table 2) due to the poor approximation of the asymmetric goethite spectrum by a single sextet. In contrast, the field distribution gave consistent values close to the correct ratio (27% as hematite for this mixture). The  $\chi^2$  values were also consistently lower for the distribution fits at  $T \geq 40$  K. The calculated  $\epsilon = 1.11$  was lower than that for either the 50% or 75% hematite mixture.

Attempts to fit a 3% hematite mixture using two sextets were unsuccessful. The small hematite peaks on the outer edge of the goethite peaks were not observed. As shown in Figure 4, the field distribution method fit the 80 K spectrum, and the resulting probability histogram (Figure 5) clearly separated the small but well-defined, high-field peak due to hematite, even though hematite was presumably absent. The R.A.H.

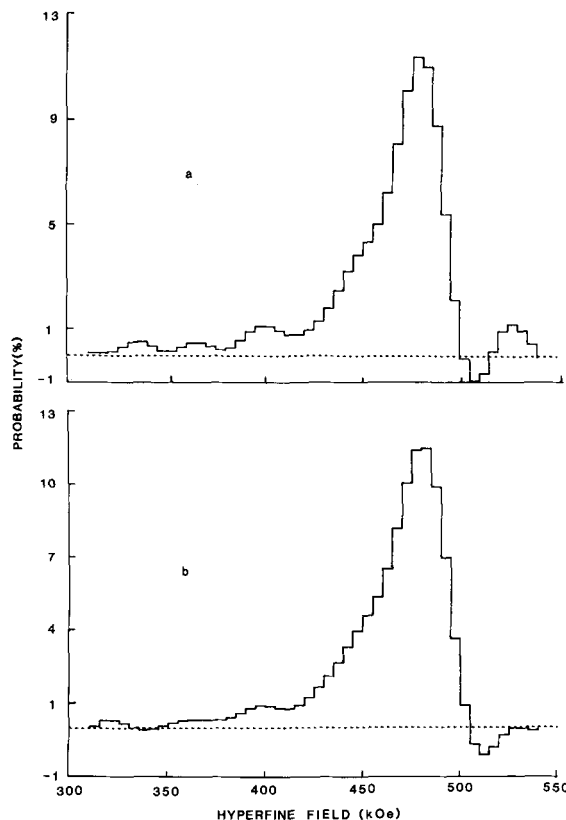


Figure 5. Probability distribution for the 3% hematite in goethite at 80 K, with a single distribution assumed, compared to the distribution obtained from pure aluminous goethite. (a) 3% hematite, (b) goethite.

values for this mixture analyzed as two distributions (Table 2) had a statistical spread of  $\sim 1\%$ , but did not change consistently with temperature. The average calculated value of  $\epsilon$  was 1.2; the analysis here also underestimated the true 3.4% Fe as hematite.

Mössbauer spectra for the individual goethite and hematite components were obtained at 14 K and several temperatures between 14 K and RT (Tables 3 and 4). Fysh and Clark (1984) suggested that the Mössbauer spectra of aluminous goethite, hematite, and mixtures of these phases should be fit using a pseudo-Lorentzian line shape, in which the intensity varies with velocity as  $(v - v_0)^{-\alpha}$ ,  $\alpha$  being an adjustable parameter exactly equal to 2 for a Lorentzian line. In addition to a Lorentzian sextet and a field distribution, Tables 3 and 4 list results for a pseudo-Lorentzian fit. These data gave  $\alpha = 2.3$ – $2.5$  and showed a slight improvement over the Lorentzian fit for goethite (Table 3) and considerable improvement for hematite (Table 4), especially at lower temperature. Fysh and Clark (1984) discussed results at 4 K only, at which temperature the lines should be symmetric. The pseudo-Lorentzian fit was not expected to duplicate the asymmetric line broadening observed both for aluminous goethite and hematite as



Table 3. Mössbauer parameters for aluminous goethite (18.6 mole % Al).<sup>1</sup>

T (K)	One sextet				$\chi^2$	PSI <sup>2</sup>		FD <sup>3</sup>
	$\delta$ (mm/s)	$\Delta$ (mm/s)	$\Gamma$ (mm/s)	H (kOe)		$\alpha$	$\chi^2$	$\chi^2$
14	0.37	-0.26	0.50	493	1690	2.36	1340	667
40	0.37	-0.25	0.60	486	2365	2.40	2103	705
80	0.36	-0.27	0.79	470	3097	2.46	2844	664
165	0.33	-0.27	1.37	403	1968	2.09	1958	977
295	0.24	0.54	0.37	0	1072	—	—	—

<sup>1</sup> Absorber had 9 mg Fe/cm<sup>2</sup>.  $\Gamma$  is peak width at half-maximum for the outermost lines of the sextet,  $\delta$  the isomer shift relative to Co(Rh) at room temperature,  $\Delta$  the quadrupole interaction.

<sup>2</sup> Pseudo-Lorentzian fit with adjustable exponent  $\alpha$  (Fysh and Clark, 1984).

<sup>3</sup> Field distribution from 310–510 kOe ( $T \leq 80$  K) or 250–450 kOe ( $T = 165$  K) in steps of 5 kOe.

temperature increased. The field distribution gave much better fits for goethite at 14 K and higher temperatures than either Lorentzian or pseudo-Lorentzian (Table 3). The field distribution gave a poorer fit for hematite at 14 K than assuming a single Lorentzian or pseudo-Lorentzian sextet (Table 4). Only at RT, where the hematite lines become appreciably broadened, did the field distribution give appreciably lower value of  $\chi^2$ . These results agreed qualitatively with results for the mixtures (Table 2), in which the field distribution improved the fit most dramatically for mixtures containing excess goethite.

The variation of isomer shift with temperature was used to estimate the recoil-free fraction  $f$  for both goethite and hematite. Assuming a Debye model for the solid gives (Heberle, 1971):

$$\delta_0 - \delta = \frac{9k\Gamma}{2mc} \left( \frac{\Gamma}{\theta} \right)^3 \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1}. \quad (2)$$

Also:

$$\ln f = -\frac{6R}{k\theta} \left[ \frac{1}{4} + \left( \frac{\Gamma}{\theta} \right)^2 \int_0^{\theta/T} \frac{x dx}{e^x - 1} \right]. \quad (3)$$

In these equations  $k$  is Boltzmann's constant,  $m$  is the mass of the <sup>57</sup>Fe nucleus,  $c$  is the speed of light,  $R$  is the recoil energy of the <sup>57</sup>Fe nucleus, and  $\theta$  is the effective Debye temperature of the solid. Heberle (1971) reported series expansions for evaluating the integrals in Eqs. (2) and (3). For goethite (Table 3) and hematite (Table 4), the average value of isomer shift for  $T \leq 80$  K was taken as  $\delta_0$ . The differences  $\delta_0 - \delta$  for 165 and 295 K were then compared with calculated values using Eq. (2) and various values of  $\theta$ . This method gave  $\theta = 500 \pm 50$  K for both goethite and hematite. Eq. (3) was used to calculate the recoil-free fractions,  $f \cong 0.93$  at  $T \leq 80$  K and  $f \cong 0.84$  at 295 K. These values are in reasonable agreement with values at 4 K reported by Fysh and Clark (1982a, 1982b) of  $f = 0.89 \pm 0.02$

Table 4. Mössbauer parameters for aluminous hematite (17.1 mole % Al).<sup>1</sup>

T (K)	One sextet				$\chi^2$	PSL <sup>2</sup>		FD <sup>3</sup>
	$\delta$ (mm/s)	$\Delta$ (mm/s)	$\Gamma$ (mm/s)	H (kOe)		$\alpha$	$\chi^2$	$\chi^2$
14	0.35	-0.20	0.37	530	915	2.3	745	1130
40	0.35	-0.20	0.38	529	857	2.4	656	991
80	0.35	-0.18	0.39	527	842	2.4	678	782
165	0.33	-0.19	0.44	519	1019	2.4	866	827
295	0.26	-0.19	0.58	496	1660	2.5	1567	985

<sup>1</sup> Absorber had 5 mg Fe/cm<sup>2</sup>.  $\Gamma$  is peak width at half-maximum for the outermost lines of the sextet,  $\delta$  the isomer shift relative to Co(Rh) at room temperature,  $\Delta$  the quadrupole interaction.

<sup>2</sup> Pseudo-Lorentzian fit with adjustable exponent  $\alpha$  (Fysh and Clark, 1984).

<sup>3</sup> Field distribution from 510–540 kOe (14, 40 K), 500–540 kOe (80 K), 500–535 kOe (165 K) or 465–515 kOe (295 K) in steps of 5 kOe.

for goethite (18.7% Al) and  $f = 0.85 \pm 0.05$  for hematite (14% Al). According to the thin absorber approximation, the total peak area of a given sample should have varied with temperature as the recoil-free fraction. Thus, the above result predicts a constant peak area for  $T \leq 80$  K and a peak area at 295 K reduced by the factor  $0.84/0.93 = 0.90$ . The total peak area in fact changed by less than 4% for both goethite and hematite in the temperature range 14–80 K. At 295 K the peak area for hematite was reduced to 0.89 of the area at 14 K. The peak area for goethite was reduced to 0.64 of the area at 14 K. The latter sample had a doublet spectrum at 295 K, however, and consequently greater thickness saturation. Using reported saturation corrections (Lang, 1963) and the  $f$  values above, the ratio of doublet peak area for goethite at 295 K to sextet peak area at 14 K was calculated to be  $\sim 0.60$ , in good agreement with the measurement. These results show that  $\epsilon$  (Eq. (1)) should be 1.0 and that the observed values of 1.1–1.3 were not due to differences in recoil-free fraction.

## CONCLUSIONS

For the quantitative determination of goethite-hematite mixtures by Mössbauer spectroscopy, liquid nitrogen spectra at  $\sim 80$  K appeared to be as satisfactory as spectra obtained at lower temperature provided the spectra were analyzed by a distribution of magnetic hyperfine fields. The observed ratios of hematite to goethite were different from the correct ratios, but not by more than 30%. For the mixtures 75%, 50%, and 25% hematite the observed  $\epsilon$  values decreased. This decrease does not mean that the actual  $\epsilon$  varied with composition, but that even using the field distribution analysis hematite was underestimated or goethite was overestimated, due in part to a thickness effect. The peak areas were proportional to the iron content only

for a thin absorber. Finite thickness produced a saturation effect which was more important for the component in excess; however, the 50–50 mixture of goethite and hematite, which should have been closest to the correct value, had  $\epsilon = 1.17$  rather than  $\epsilon = 1.00$ , as predicted by results from the individual components. The field distribution fitting procedure underestimated the hematite contribution for all proportions of mixture, but by less than a two-sextet fitting method. The presence of 3% hematite in aluminous goethite could be detected easily using the field distribution. Spectra at 80 K gave as much mineralogical information as those obtained at lower temperature if a field distribution was used for fitting. Lower temperature spectra should be obtained, however, if a doublet is present in the 80 K spectrum, in order to characterize the doublet component.

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