A Precise Iron-57 Mössbauer Spectroscopic Study of Iron(III) in the Octahedral and Channel Sites of Akaganéite (β-Iron Hydroxide Oxide)

By **James H. Johnston** * and **Nicholas E. Logan**, Chemistry Department, Victoria University of Wellington, Private Bag, Wellington, New Zealand

The ^{57}Fe Mössbauer spectra of β-FeO(OH) (akaganéite), prepared by two different methods and subjected to different washing procedures, have been determined under conditions of higher resolution than those previously reported. The spectra recorded at room temperature have been resolved, using a computer-based curve-fitting procedure, into two closely overlapping quadrupole-split iron(III) doublets, rather than the single doublet reported previously. The inner doublet having an average value of the quadrupole interaction Δ = 0.545 mm s^{-1} and isomer shift δ = 0.155 mm s^{-1} arises from Fe^{3+} in the Fe(O,OH)$_6$ octahedra of the β-FeO(OH) lattice. The outer doublet having Δ = 0.927—0.959 mm s^{-1} and an average value of δ = 0.157 mm s^{-1} probably arises from Fe^{3+} in the channels within the unit cells, with the range of Δ values presumably being due to variation in the Cl$^-$, [OH]$^-$, and H$_2$O content in these channels.

In recent years many workers have reported the ^{57}Fe Mössbauer spectrum of synthetic and natural (the mineral akaganéite) β-FeO(OH).[1-9] Although, at room temperature, the Mössbauer spectrum of β-FeO(OH) appears to be a typical quadrupole-split iron(III) doublet, the majority of the previous spectra were recorded over a wide velocity range, and computer-based spectral curve-fitting procedures were not employed. This has resulted in variations in the isomer-shift (δ) and quadrupole-interaction (Δ) values, together with reasonably large errors associated with these (Table 1). In addition, recent computer-based Mössbauer spectroscopic and in some cases *X*-ray diffraction studies have suggested that akaganéite is a form of secondary iron in soils,[10] corrosion products,[11-13] and marine manganese nodules.[14] The Mössbauer results from these studies also differ from those of the former workers.

In view of these discrepancies it was decided to prepare β-FeO(OH) synthetically, record the Mössbauer spectrum over a narrow velocity range to achieve good resolution, and analyse it with the help of computer-based curve-fitting procedures. This paper reports the results of such a study.

TABLE 1

Literature values for the isomer shift (δ) and quadrupole interaction (Δ) for β-FeO(OH)

Δ/mm s^{-1}	δ [a]/mm s^{-1}	Ref.
0.62 ± 0.06	0.11 ± 0.06	1
0.72 ± 0.10	0.16 ± 0.04	2
0.70 ± 0.08	0.12 ± 0.02	3
0.700 ± 0.008	0.157 ± 0.018	4
0.70 ± 0.08	0.12 ± 0.02	5
0.40 ± 0.01	0.09 ± 0.01	6
0.62 ± 0.02	0.17 ± 0.02	7
0.7	0.14	8
0.68 ± 0.02	0.40 ± 0.01 [b]	9

[a] With respect to copper. [b] Source matrix not quoted.

EXPERIMENTAL

Preparation.—The compound β-FeO(OH) was prepared by hydrolysis of 0.1 mol dm^{-3} FeCl$_3$ solution at 80 °C for 6 h.[15-17] The resulting precipitate was washed many times over 8 d by decantation using distilled water made slightly alkaline with ammonia to prevent peptization.[15] Samples with withdrawn after 1 d (sample 1) and after 8 d (sample 2), separated by centrifugation, and dried. In addition, samples of β-FeO(OH) prepared by the method of Atkinson *et al.*[18] were obtained.[19] In this the Cl$^-$ was removed by dialysis rather than washing as above. Samples 3 and 4 were withdrawn from the colloidal solution after *ca.* 4 and 12 weeks of dialysis respectively, and evaporated at room temperature to produce solid β-FeO(OH).

The chloride content of all the samples was determined by colorimetric analysis using mercury(II) thiocyanate. In both cases, *X*-ray diffraction and i.r. spectroscopy showed that β-FeO(OH) was the only phase present. Line broadening of the *X*-ray diffraction peaks was used for a comparative estimate of the crystallite particle sizes for each sample.[20]

Mössbauer Spectroscopy.—Iron-57 Mössbauer spectra were obtained using a 400-channel constant-acceleration Mössbauer spectrometer equipped with a nominal 10 mCi ^{57}Co source in a copper matrix.[21] All the spectra were initially recorded at room temperature over a narrow velocity range of ±1.8 mm s^{-1}. For this the velocity scale was calibrated with a sodium pentacyanonitrosylferrate dihydrate absorber.[22] The isomer shifts are quoted here with respect to the copper source. The spectrum of sample 3 was also recorded at liquid-nitrogen temperature (77 K) over a wider velocity range of ±9 mm s^{-1}. Natural iron was used to calibrate the velocity scale for this spectrum.[23]

All the spectra were accumulated until peak absorptions (peak heights) typically of the order 8×10^5—9×10^5 counts were obtained. To avoid line-broadening effects due to excessive sample thickness, all the samples contained 8 mg of Fe per cm^2 of sample area.[22] A number of Lorentzian peaks were computer-fitted to the experimental spectra using a modified version of the χ^2 non-linear regression minimisation procedure of Stone.[24] The ' acceptability of the fit ' was evaluated on both chemical and statistical grounds. For the fit to be chemically acceptable the widths and areas of the peaks defining a respective quadrupole-split spectrum had to be similar, and the isomer-shift and quadrupole-interaction values consistent with those commonly obtained for similar Fe^{3+} resonances. For statistical acceptability, the χ^2 value (weighted sum of the difference of squares) should lie between the 1 and 99% points on the χ^2 probability curve.[22] In addition, the plot of residual deviation (differences between the experimental and calculated intensity values against the velocity) should be statistically featureless within ±3 standard deviation units in the intensity scale.

The errors quoted for the position, width, and relative area parameters were derived from the variance–covariance matrix computed in the fitting procedure. The errors in the Δ and δ values are simply the root-mean-square values of the errors in the position parameters for the respective peaks defining the quadrupole-split spectrum.

RESULTS AND DISCUSSION

The *X*-ray diffraction line broadening showed that the samples prepared by the method of Gallagher and Phillips[15] and Mackay[16] have a much larger particle size than those prepared by that of Atkinson *et al.*[18] In the former method the β-FeO(OH) settled out from solution, while in the latter it remained in a colloidal form until it separated by evaporation. The analytical data (Table 2) show that the Cl^- is slowly removed by washing and that even after long washing periods complete removal is not effected. A similar conclusion was reached by Ellis *et al.*[25] who found that it was extremely difficult to reduce the Cl^- content below 2%.

The room-temperature Mössbauer spectra of all the samples were similar and appeared to be a iron(III) doublet with notable asymmetry on the outer side of each peak [see Figure 1 (*a*)]. Since the computer curve-fitting analysis and results for the spectra of all the samples were also similar, only that for sample 3 is now discussed.

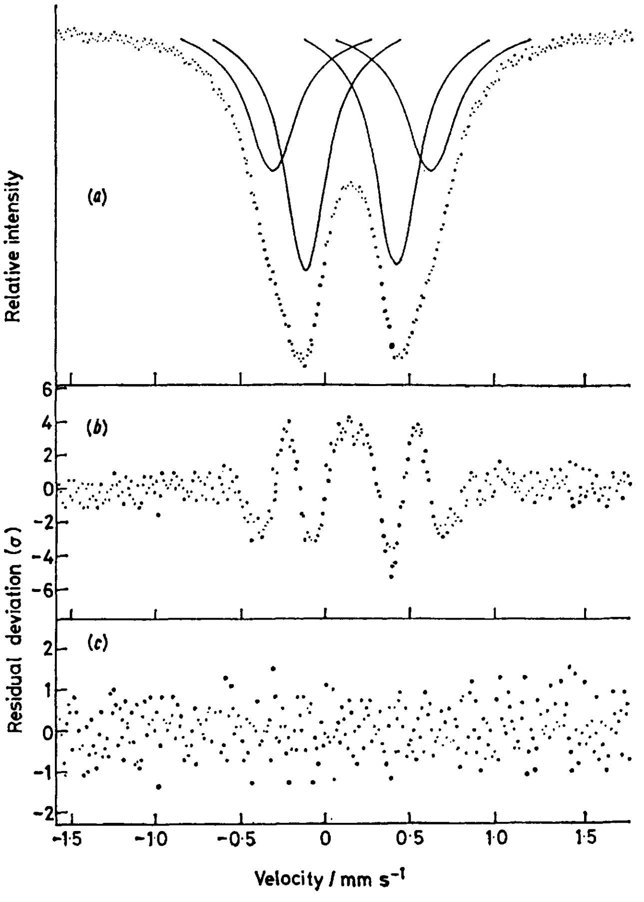

FIGURE 1 (*a*) Iron-57 Mössbauer spectrum recorded at room temperature for β-FeO(OH), sample 3. The bar represents ±1 σ in the intensities. (*b*) and (*c*) Plot of residual deviations after a two-peak and a four-peak fit, respectively

An initial two-peak fit of the spectrum of sample 3 converged to give an unacceptably high $\chi^2 = 2\,261$ (the 1 and 99% points having $\chi^2 = 422$ and 298 respectively), and a plot of the residual deviation showed the presence of another two peaks [Figure 1 (*b*)]. The peak parameters and δ and Δ values are shown in Table 2. An ensuing four-peak fit converged with an acceptable $\chi^2 = 320$ (the 1 and 99% points having $\chi^2 = 416$ and 292 respectively) and a statistically featureless (within $\pm 3\sigma$) plot of the residual deviations [Figure 1 (*c*)]. The peak parameters for this fit are also shown in Table 2. A six-peak fit was attempted but this was unsuccessful, resulting in divergence of the fitting process, thus suggesting that the spectrum comprises only four peaks. A consideration of the peak widths and areas shows that the Mössbauer spectrum of β-FeO(OH) consists of two closely overlapping outer (peaks 1 and 4) and inner (peaks 2 and 3) quadrupole-split iron(III) doublets, having similar isomer shifts but differing quadrupole-interaction values. A similar set of two doublets was successfully fitted to each of the other three spectra (Table 2).

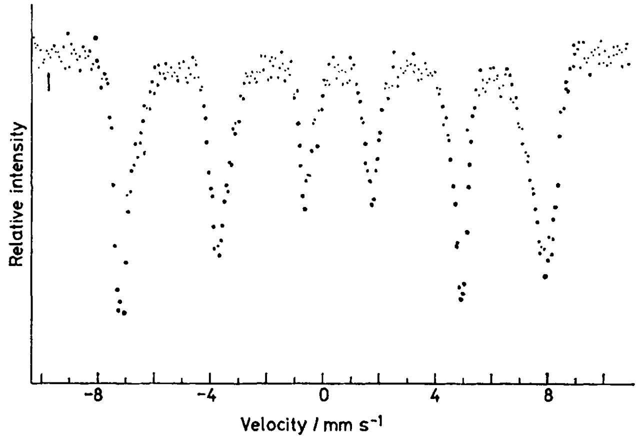

FIGURE 2 Iron-57 Mössbauer spectrum of β-FeO(OH) recorded at 77 K. The bar represents ±1 σ in the intensities

Since Fe^{3+} Mössbauer spectra may be broadened by magnetic-relaxation effects it is possible that the experimental room-temperature spectrum of akaganéite could be interpreted in this manner as an alternative to the two non-equivalent Fe^{3+} sites. However, with increasing relaxation time (and hence peak broadening) the quadrupole peak corresponding to the $\pm\frac{3}{2}\rightarrow\pm\frac{1}{2}$ transition relaxes at a different rate than that corresponding to the $\pm\frac{1}{2}\rightarrow\pm\frac{1}{2}$ and $\mp\frac{1}{2}$ transitions, thus resulting in unequal widths and areas of these respective peaks.[26,27] In the experimental spectrum [Figure 1 (*a*)] the peak areas are equal and the asymmetry on the outer side of each peak is mirrored about the centre of the spectrum. Also the widths and areas of the respective computer-fitted doublet peaks show no such differential-relaxation effects. It is therefore concluded that the Mössbauer spectrum of akaganéite is best interpreted in terms of two non-equivalent Fe^{3+} sites.

The Mössbauer spectrum of sample 3 recorded at 77 K (liquid-nitrogen temperature) shows magnetic hyperfine splitting (Figure 2), typically exhibited for antiferromagnetic β-FeO(OH) below the Néel temperature.[1,6-9,28] A closer inspection of this spectrum also suggests the presence of two closely overlapping six-peak magnetic hyperfine spectra, arising from the two non-equivalent Fe^{3+} sites.

For the room-temperature spectra, the δ and Δ values of the two-peak fits correspond to those of previous workers (Table 1),[1-9] thus showing that none of those workers managed to resolve the two overlapping iron(III) resonances as has been achieved here. They have simply quoted δ and Δ values for a doublet spectrum which is actually the mean of two overlapping doublets. The question now arises as to which sites are occupied by Fe^{3+} to produce this Mössbauer spectrum.

The compound β-FeO(OH) has a hollandite (α-MnO_2) type structure consisting of $Fe(O,OH)_6$ octahedra linked to form double strings parallel to the *c* axis.[8,16,29] This results in the channel-type structure shown in Figure 3. These channels have a diameter range of 3—5 Å and generally contain Cl^- ions which stabilize the akaganéite lattice.[15,16,18] These can be replaced by $[OH]^-$ or H_2O with progressive washing.[8,15,16,18]

The δ and Δ values for the inner doublets of all the room-temperature spectra are very similar and comparable to that of superparamagnetic goethite, α-FeO(OH).[6,28,30-32] Also, since the peaks of this doublet are significantly narrower than those of the outer doublet, the former must arise from Fe^{3+} in a well defined (ordered) crystallographic site. The inner doublet is therefore assigned to Fe^{3+} in the $Fe(O,OH)_6$ octahedra of the lattice.

TABLE 2

Computer-fitted Mössbauer data for β-FeO(OH)

Sample no.	Wt. % of Cl^-	Peak no.	Position (mm s^{-1})	Width (mm s^{-1})	Relative area
3	5.4	1	−0.184 ± 0.002	0.443 ± 0.005	1.00
		2	0.491 ± 0.002	0.447 ± 0.004	0.99 ± 0.01
		Δ = 0.675 ± 0.003, δ = 0.154 ± 0.003 mm s^{-1}			
3	5.4	1	−0.315 ± 0.008	0.360 ± 0.013	1.00
		2	−0.116 ± 0.004	0.307 ± 0.009	1.44 ± 0.008
		3	0.421 ± 0.004	0.301 ± 0.009	1.38 ± 0.07
		4	0.622 ± 0.008	0.373 ± 0.013	1.03 ± 0.07
		Peaks 1 and 4, Δ = 0.937 ± 0.012, δ = 0.154 ± 0.012 mm s^{-1}			
		Peaks 2 and 3, Δ = 0.537 ± 0.012, δ = 0.153 ± 0.012 mm s^{-1}			
1	6.9	1	−0.321 ± 0.007	0.330 ± 0.016	1.00
		2	−0.112 ± 0.004	0.289 ± 0.013	1.21 ± 0.09
		3	0.426 ± 0.004	0.284 ± 0.011	1.26 ± 0.08
		4	0.639 ± 0.007	0.307 ± 0.016	0.85 ± 0.08
		Peaks 1 and 4, Δ = 0.959 ± 0.009, δ = 0.159 ± 0.009 mm s^{-1}			
		Peaks 2 and 3, Δ = 0.536 ± 0.006, δ = 0.156 ± 0.006 mm s^{-1}			
2	3.5	1	−0.314 ± 0.009	0.366 ± 0.015	1.00
		2	−0.129 ± 0.004	0.287 ± 0.011	1.09 ± 0.09
		3	0.424 ± 0.004	0.282 ± 0.011	1.03 ± 0.08
		4	0.613 ± 0.008	0.359 ± 0.014	1.03 ± 0.09
		Peaks 1 and 4, Δ = 0.927 ± 0.012, δ = 0.149 ± 0.012 mm s^{-1}			
		Peaks 2 and 3, Δ = 0.553 ± 0.006, δ = 0.149 ± 0.006 mm s^{-1}			
4	4.5	1	−0.312 ± 0.006	0.337 ± 0.012	1.00
		2	−0.116 ± 0.003	0.307 ± 0.007	1.79 ± 0.05
		3	0.436 ± 0.003	0.300 ± 0.006	1.79 ± 0.05
		4	0.646 ± 0.006	0.341 ± 0.011	0.96 ± 0.05
		Peaks 1 and 4, Δ = 0.958 ± 0.009, δ = 0.167 ± 0.009 mm s^{-1}			
		Peaks 2 and 3, Δ = 0.552 ± 0.004, δ = 0.160 ± 0.004 mm s^{-1}			

The δ and Δ values for the outer doublet vary significantly more between respective samples than do those for the inner doublet. This together with the larger peak widths suggests that the Fe^{3+} giving rise to this resonance occupies a less well defined site. Since the hollandite structure has no other possible lattice sites which Fe^{3+} can occupy,[8,16,29] this outer doublet could arise from Fe^{3+} in the channel sites within the structure, with excess of $[OH]^-$ or Cl^- ions serving to balance the charges.

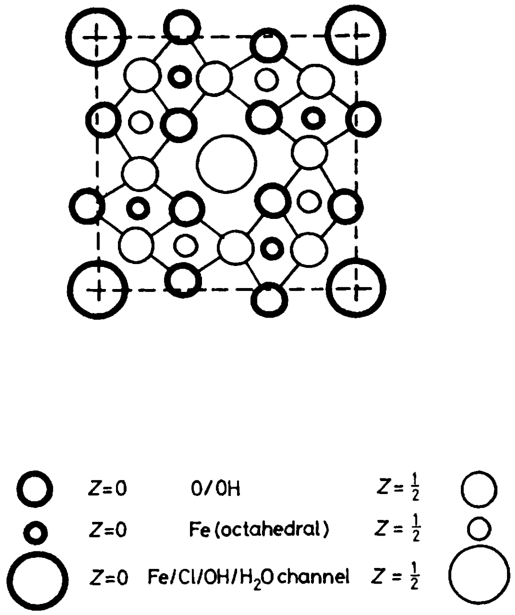

FIGURE 3 A projection on to the 001 plane of the unit cell of the hollandite structure upon which the structure of β-FeO(OH) is based. $a = 10.48$, $c = 3.023$ Å, Tetragonal, space group $I4/m$ (refs. 8, 16, and 29)

From the results presented here, it is difficult to deduce any correlation between the Δ value for the outer doublet and the residual amount of Cl^- ions in the β-FeO(OH) lattice. However, the smallest such Δ value does correspond to the lowest Cl^- content (sample 2), although the converse does not hold. It seems reasonable to expect the Cl^- ions adjacent to the Fe^{3+} ions in the channels to exert a stronger electric field on the Fe^{3+}, thereby producing a larger quadrupole splitting than either $[OH]^-$ or H_2O. Hence, with progressive washing, the Δ value would decrease. Also it is of interest to note that akaganéite from the high-chloride volcanic environment of White Island, New Zealand, has values of $\Delta = 0.959$ mm s^{-1},[11] corresponding to those of highest Cl^- content studied here.

We thank Dr. R. L. Parfitt for supplying the fine-particle-size β-FeO(OH) samples, K. E. Knedler and J. B. Metson for their assistance in the initial phase of this study, and Drs. C. W. Childs and B. A. Goodman for their interest and comments on this manuscript.

[7/1997 *Received, 14th November, 1977*]

REFERENCES

[1] M. J. Rossiter and A. E. M. Hodgson, *J. Inorg. Nuclear Chem.*, 1965, **27**, 63.

[2] C. L. Herzenberg and D. Toms, *J. Geophys. Res.*, 1966, **71**, 2661.

[3] I. Dézsi, L. Keszthely, D. Kulgawczuk, B. Moinár, and N. A. Eissa, *Phys. Stat. Sol.*, 1967, **22**, 617.

[4] J. H. Terrell and J. J. Spijkerman, *Appl. Phys. Letters*, 1968, **13**, 11.

[5] D. S. Kulgawczuk, *Nukleonika*, 1969, **14**, 777.

[6] H. Kubsch, E. Fritzsch, and H. Baum, *Krist. Tech.*, 1972, **7**, K77.

[7] P. O. Voznyuk and V. N. Dubinin, *Fiz. Tverd. Tela*, 1973, **15**, 1897.

[8] A. T. Howe and K. J. Gallagher, *J.C.S. Faraday I*, 1975, 22.

[9] D. Hanzel and F. Sevsek, *J. de Phys.*, 1976, **37**, C6.

[10] N. E. Logan, J. H. Johnston, and C. W. Childs, *Austral. J. Soil Res.*, 1976, **14**, 217.

[11] J. H. Johnston, *Geochim. Cosmochim. Acta*, 1977, **41**, 539.

[12] J. H. Johnston, J. B. Metson, C. W. Childs, and H. R. Penhale, *Austral. J. Soil. Res.*, 1978, in the press.

[13] L. A. Taylor, H. K. Mao, and P. M. Bell, *Proc. Fifth Lunar Conf. Suppl.* 5, *Geochim. Cosmochim. Acta*, 1974, **1**, 743.

[14] J. H. Johnston and G. P. Glasby, *Geochem. J.*, 1978, in the press.

[15] K. J. Gallagher and D. N. Phillips, *Chimia*, 1969, **23**, 465.

[16] A. L. Mackay, *Mineral Mag.*, 1960, **32**, 545.

[17] H. B. Weiser and W. O. Milligan, *J. Amer. Chem. Soc.*, 1935, **57**, 238.

[18] R. J. Atkinson, A. M. Posner, and J. P. Quirk, *Clays and Clay Mineral.*, 1977, **25**, 49.

[19] R. L. Parfitt, Soil Bureau, D.S.I.R., Lower Hutt, New Zealand, personal communication.

[20] H. P. Klug and L. E. Alexander, *X*-Ray Diffraction Procedures, Wiley, New York, 1954.

[21] J. H. Johnston and J. E. A. Nixon, *New Zealand J. Sci.*, 1971, **14**, 1107.

[22] G. M. Bancroft, 'Mössbauer Spectroscopy: An Introduction for Inorganic Chemists and Geochemists,' McGraw-Hill, London, 1973.

[23] National Bureau of Standards, *Tech. News Bull.*, 1972, **56**, 138.

[24] A. J. Stone, Appendix to G. M. Bancroft, A. G. Maddock, W. Ong, and R. H. Prince, *J. Chem. Soc.* (*A*), 1967, 1966.

[25] J. Ellis, R. Giovanoli, and W. Stumm, *Chimia*, 1976, **30**, 194.

[26] M. Blume, *Phys. Rev. Letters*, 1965, **14**, 96.

[27] H. H. Wickman and G. K. Wertheim, 'Chemical Applications of Mössbauer Spectroscopy,' eds. V. I. Goldanskii and R. H. Herber, Academic Press, New York, 1968, ch. 11.

[28] T. Takada, M. Kiyama, Y. Bando, and T. Shinjo, *Bull. Inst. Chem. Res. Kyoto Univ.*, 1969, **47**, 298.,

[29] K. J. Gallagher, *Nature*, 1970, **226**, 1225.

[30] T. Shinjo, *J. Phys. Soc. Japan*, 1966, **21**, 917.

[31] A. M. Van Der Kraan and J. J. Van Loef, *Phys. Letters*, 1966, **20**, 614.

[32] N. Yamamoto, T. Shinjo, M. Kiyama, Y. Bando, and T. Takada, *J. Phys. Soc. Japan*, 1968, **25**, 1267.