

The influence of crystallinity on the Mössbauer spectrum of lepidocrocite

ENVER MURAD AND UDO SCHWERTMANN

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

ABSTRACT. Particle morphology can result in very pronounced effects of crystallinity on the Mössbauer spectra of lepidocrocite. Such effects can noticeably increase the quadrupole splitting of poorly crystallized paramagnetic lepidocrocites, making it necessary to fit two doublets of different quadrupole splittings to Mössbauer spectra of such samples, and may lower the onset of magnetic ordering from the bulk Néel temperature of 77 ± 1 K to about 50 K.

At 4.2 K, distributions of magnetic hyperfine fields with a limiting upper field of 460 kOe are observed. The contributions of lower fields to such distributions increase with decreasing crystallinity, producing asymmetrically broadened resonant lines.

LEPIDOCROCITE (γ -FeOOH) has a crystal structure based on distorted, iron-centered octahedra arranged in two-dimensional layers normal to the crystallographic *b*-axis (Ewing, 1935). In the paramagnetic state, Mössbauer spectra of lepidocrocite consist of a quadrupole-split doublet, the parameters of which ($\Delta E_Q = 0.55$ mm s⁻¹, $\delta/Fe = 0.35$ mm s⁻¹) are not significantly different from those of other paramagnetic oxides of trivalent iron, e.g. goethite (Bowen, 1979). Yamamoto (1968) and Johnson (1969) reported somewhat different Néel temperatures, T_N , of 50 and 73 K, respectively, for lepidocrocite. Johnson (1969) also noted that the onset of magnetic order is not immediate on lowering the temperature below T_N , but that both a doublet and a sextet coexist over a temperature range of about 10 K in which the sextet only gradually replaces the doublet. The hyperfine fields, H_i , observed by Yamamoto (1968) and Johnson (1969) at 4.2 K (470 and 460 kOe, respectively) are quite similar. These hyperfine fields are distinctly lower than those of hematite (544 kOe) and goethite (505 kOe), so that this parameter can readily serve to distinguish between these minerals. On the basis of the above hyperfine field values for lepidocrocite, some overlap with Mössbauer spectra of ferrihydrite at 4.2 K (H_i between 470 and 500 kOe; Murad and Schwertmann, 1980; Murad,

1982a; Schwertmann *et al.*, 1982) is, however, conceivable. This possibility will be discussed in more detail below.

Johnson (1969) took Mössbauer spectra of a synthetic and a well-crystallized neutral lepidocrocite between room temperature and 4.2 K. Significant differences between the Mössbauer spectra of these samples in the vicinity of the Néel temperature indicate that crystallinity may play a major role in determining the magnetic properties of lepidocrocite.

To assess the influence of crystallinity, the present study was carried out on two synthetic lepidocrocites of different particle sizes and morphologies. Mössbauer spectra of these samples were run at room temperature, between 85 and 50 K, and at 4.2 K.

Experimental. Synthetic lepidocrocites were prepared by bubbling O₂ through 0.2 M aqueous FeCl₂ solutions at pH 7.4–7.5 and ambient temperature (sample P23). One such lepidocrocite was subsequently treated for 568 hours with 1 M KOH solution containing $3.32 \cdot 10^{-1}$ M Si at 80 °C (sample 22/568; Schwertmann and Taylor, 1972). This treatment resulted in a drastic change of morphology, the originally ragged crystals (fig. 1a) attaining a compact, more or less rectangular appearance (fig. 1b). Schwertmann and Taylor (1972) found 568 hours of Si/KOH-treatment ('ripening process') to reduce the surface area of the original sample P22 from 58 m²/g to 19 m²/g, and XRD line half-widths from 0.45 to 0.25 °2 θ . XRD indicated both P23 and 22/568 to consist exclusively of lepidocrocite. Data characterizing the crystallinities of the samples are given in Table I.

The Mössbauer spectrometer comprised a ⁵⁷Co/Rh source driven in a sinusoidal mode. Between 85 and 50 K the absorber only was cooled in a cold-finger cryostat, and at 4.2 K both source and absorber were cooled using liquid helium in a bath cryostat. Data were accumulated in a 1024 channel analyser and, after folding, computer-fitted

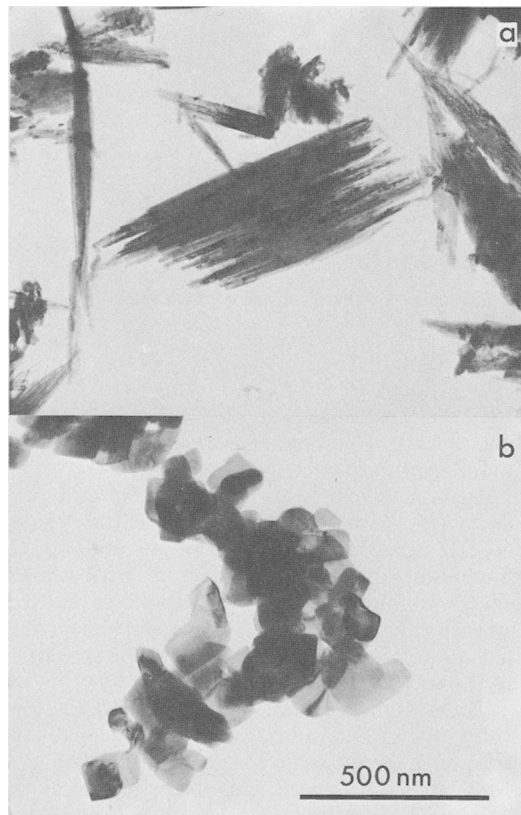


FIG. 1. Electron micrographs of synthetic lepidocrocites (a) P23 and (b) 22/568.

with Lorentzians. In the fitting procedure, the lines of doublets were constrained to have equal widths; opposite lines of sextets to have equal widths and intensities. Hyperfine field distributions were calculated using a model-free procedure described by Murad (1982b). A 6 μm iron foil served for velocity calibration and as isomer shift reference.

Results. Room-temperature Mössbauer spectra of both lepidocrocites consisted of a quadrupole-split doublet (fig. 2). A two-Lorentzian fit to the room temperature spectrum of the untreated sample P23 gave a higher quadrupole splitting ΔE_Q of 0.550 mm s^{-1} than the spectrum of the Si/KOH-treated sample 22/568, which had $\Delta E_Q = 0.527 \text{ mm s}^{-1}$. P23 also had wider lines than 22/568 (0.311 vs. 0.256 mm s^{-1} , respectively). Since identical sample quantities were used for both spectra, and Fe concentrations were sufficiently low (3.5 mg Fe/cm^2), saturation effects can be ruled out.

A reconnaissance study of the magnetic behaviour of sample 22/568 was carried out in the vicinity of the expected Néel temperature by

TABLE I. Data characterizing the crystallinities of the studied lepidocrocites P23 and 22/568

Sample	Fe_o/Fe_t ^a	S [†] m^2/g	MCD[0k0] [‡] nm
P23	0.40	65	19
22/568	0.06	18	66

^a Ratio of oxalate soluble to total Fe
[†] Surface area determined by EGME
[‡] Calculated from XRD line broadening using the Scherrer formula

measuring the intensity of the 14.4 keV γ -ray transmitted with the Mössbauer drive kept static, i.e. at zero velocity, between 85 and 56 K (fig. 3). The γ -ray intensity vs. temperature curve becomes steeper below 77 K, but begins to level out again below about 65 K. Mössbauer spectra taken at selected temperatures in this region offer an explanation for this behaviour. Down to 74 K, Mössbauer spectra of sample 22/568 show only a quadrupole-split doublet. Average widths of two Lorentzians fitted to these spectra increase from 0.27 mm s^{-1} at 77 K to 0.29 mm s^{-1} at 76 K, 0.30 mm s^{-1} at 75 K, 0.33 mm s^{-1} at 74 K, and 0.39 mm s^{-1} at 72 K. The existence of a magnetically ordered component as wings on the

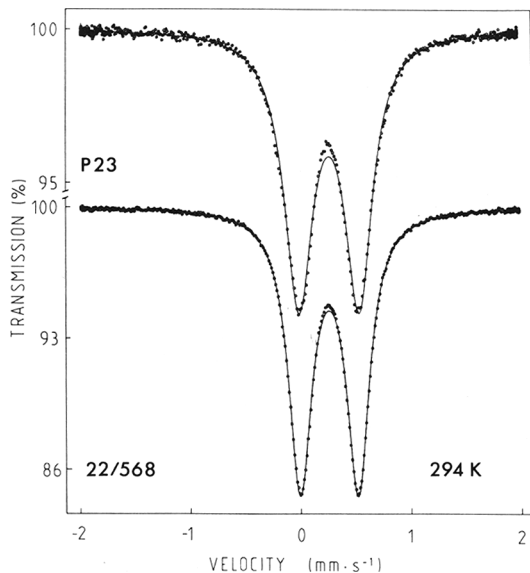


FIG. 2. Mössbauer spectra of P23 and 22/568 at room temperature fitted with one doublet each.

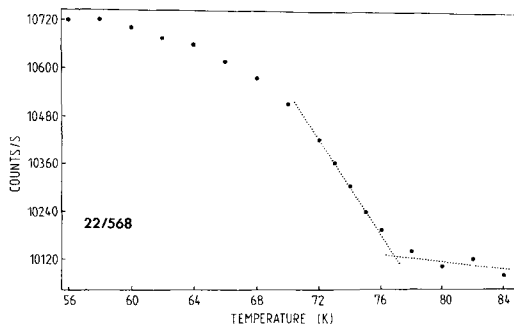


FIG. 3. 14.4 keV γ -ray transmission vs. temperature (thermal scan) in the vicinity of the Néel temperature.

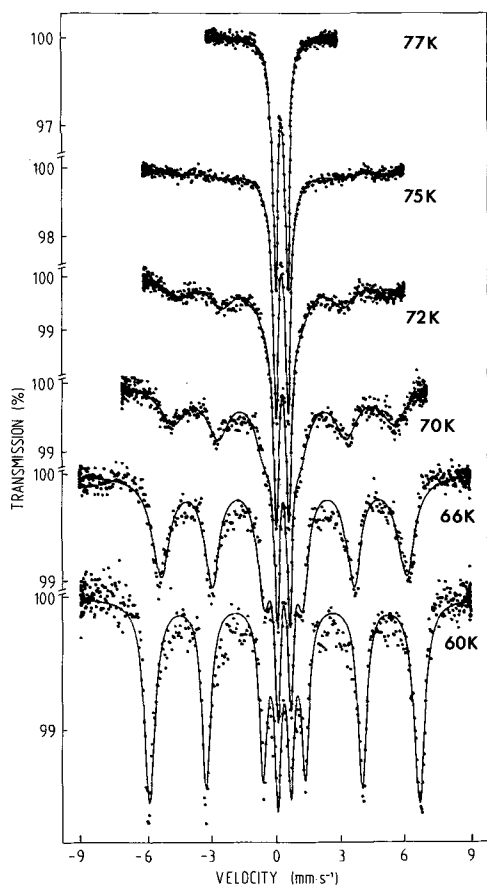


FIG. 4. Mössbauer spectra of 22/568 in the vicinity of the Néel temperature, showing gradual replacement of superparamagnetic doublet by sextet.

doublet first becomes apparent at about 72 K (fig. 4). The trend of the γ -ray transmission vs. temperature curve (fig. 3), and the increasing doublet line widths below 77 K, however, indicate magnetic

ordering to begin at 77 K. Above 72 K the magnetic hyperfine field and the degree of magnetic ordering are probably so low that magnetically ordered components are 'hidden' underneath the doublet, and only effect increased line widths. As temperature decreases below 72 K, the area of the magnetically ordered component increases at the cost of the paramagnetic doublet (fig. 4).

The Mössbauer spectra of P23 have a markedly different appearance from those of 22/568 in this temperature region. In P23 the doublet persists down to about 50 K. Line widths measured for P23 are 0.30 mm s^{-1} at 66 K, 0.32 mm s^{-1} at 60 K, and 0.38 mm s^{-1} at 50 K. A first observation of noticeably wider lines at 50 K indicates that magnetic ordering of P23 just begins between 50 and 60 K.

At 4.2 K both P23 and 22/568 show complete magnetic ordering (fig. 5). The lines of the Mössbauer spectrum of P23, however, are considerably wider than those of 22/568 ($1.09 \text{ vs. } 0.51 \text{ mm s}^{-1}$, respectively, using one-sextet fits), and both deviate from Lorentzian shape. The magnetic hyperfine fields calculated from such one-sextet fits are 445 kOe for P23 and 456 kOe for 22/568 (Table II). When the spectra are fitted with two sextets each, the outer sextets give hyperfine fields of 453 kOe for P23 and 457 kOe for 22/568. Three-sextet fits give acceptably good coincidence with the experimental data (fig. 5) and further reduce the differences between the hyperfine fields of the outer sextets,

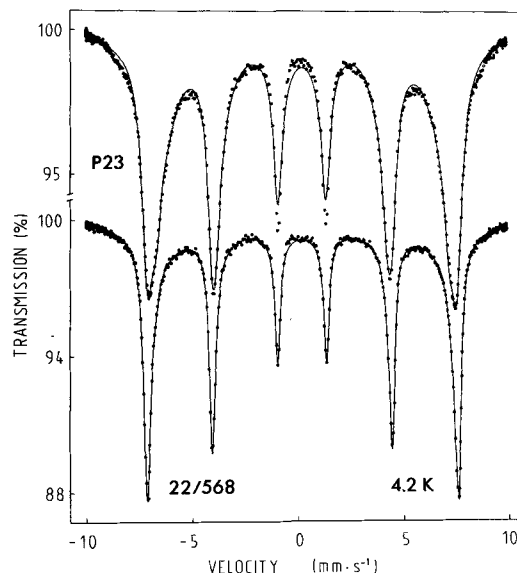


FIG. 5. Mössbauer spectra of P23 and 22/568 at 4.2 K fitted with three sextets.

which are then given by 456 kOe for P23 and 458 kOe for 22/568. Line widths of these outer sextets are 0.67 and 0.40 mm s⁻¹, respectively; see Table II.

TABLE II. Mössbauer parameters of the studied lepidocrocites at room temperature and 4.2 K

Sample	T(K)	$\delta(\text{Fe})$	ΔE_Q	FWHM	H_1	I_{rel}	
			mm·s ⁻¹		kOe		
P23	294	0.367(1)	0.550(1)	0.311(1)	-	1.00	
		0.368(1)	0.480(1)	0.252(1)	-	0.45*	
		0.365(1)	0.67(2)	0.331(1)	-	0.55*	
	4.2	0.340(4)	0.041(7)	1.09(1)	445(1)	1.00	
		0.341(2)	0.021(4)	0.67(2)	456(1)	0.27†	
22/568	294	0.367(1)	0.527(1)	0.256(1)	-	1.00	
			0.342(1)	0.018(3)	0.507(6)	456(1)	1.00
			0.343(1)	0.017(1)	0.403(4)	458(1)	0.19†
	4.2						

$\delta(\text{Fe})$ = isomer shift relative to metallic iron

ΔE_Q = quadrupole splitting

H_1 = magnetic hyperfine field

FWHM = full line width at half maximum

Numbers in parentheses give standard deviation on last digit

* Parameters of two-sextet fit to paramagnetic doublet

† Parameters of outer sextet of a three-sextet fit.

If distributions of hyperfine fields are fitted to the 4.2 K spectra (fig. 6), the fields of maximum absorption are 453 and 458 kOe, and the half-widths of these distributions 52 and 19 kOe for P23 and 22/568, respectively.

Discussion. The main difference between the lepidocrocites P23 and 22/568 is the better crystallinity of the latter. This is immediately evident from the electron micrographs, and parameters quantifying this difference (surface areas and XRD line widths) are discussed in the *Experimental* section and given in Table I.

The higher quadrupole splitting of P23 compared to that of 22/568 at room temperature (0.550 vs. 0.527 mm s⁻¹) is reminiscent of the observation that the quadrupole splitting of superparamagnetic hematite increases with decreasing crystallinity (Kündig *et al.*, 1966; Kündig *et al.*, 1967; Kraan, 1973). This higher quadrupole splitting has been attributed to increasing contributions of surface portions of the crystals, in which the oxygen octahedra would be more strongly distorted than within the crystal cores, as particle sizes decrease.

The shredded ends of the platelets that make up most of P23 result in a higher proportion of surface

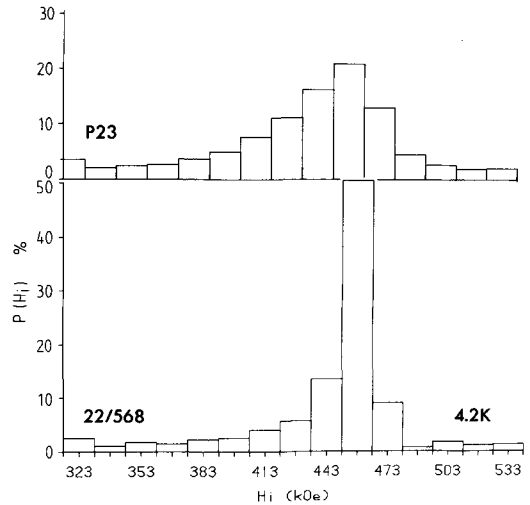


Fig. 6. Hyperfine field distributions observed for P23 and 22/568 at 4.2 K.

regions than the compact crystals of 22/568. The difference in quadrupole splittings thus is in agreement with the better crystallinity of 22/568 as compared to P23. The wider lines observed for P23 at room temperature indicate that a two-doublet fit, one doublet each for the core and outer crystal regions ('shredded fibres') [Kraan, 1973], is more appropriate for this spectrum, although even this fit might be a simplified representation of an actual distribution of quadrupole splittings (Wivel and Mørup, 1981).

The existence of a doublet plus a sextet over a wide temperature range below 73 K in 22/568, and the lack of observation of magnetic splitting in P23 down to 50 K, present a marked contrast to the behaviour of microcrystalline goethite, in which Mørup *et al.* (1983) observed the transition from a doublet to a sextet to take place within a very narrow temperature range. In spite of the good crystallinity which electron micrographs indicate 22/568 to have, the Mössbauer spectra indicate a range of Fe³⁺ environments to exist even in this sample. The spectra of 22/568 resemble those of the natural lepidocrocite described by Johnson (1969), which, possibly because this is even better crystallized than 22/568, shows complete magnetic ordering at 58 K. The persistence of a (super-) paramagnetic component in 22/568 to a comparable temperature may at least in part be due to the incorporation of some Si into this sample during the Si/KOH-treatment. A considerable proportion of P23, on the other hand, is made up of ragged, fibrous (c. 10 nm thick) ends of the platelets constituting this sample; this morphology

is probably responsible for relaxational lowering of the magnetic ordering temperature down to about 50 K.

The fitting of two or three magnetic hyperfine fields to the 4.2 K spectra corresponds essentially to a simplified hyperfine field distribution model. The limiting maximum hyperfine field of about 460 kOe seems to be the same for both studied lepidocrocites, but P23 has much higher contributions of low-field components than 22/568. This, again, is consistent with P23 having more surface Fe^{3+} -ions, whose magnetic coupling to the particle cores (Kraan, 1973) is weaker than in 22/568.

The spectra of both lepidocrocite and ferrihydrite can be interpreted in terms of distributions of magnetic hyperfine fields, resulting from distributions of environments of the resonant Fe^{3+} ions. Distributions of environments will cause magnetic exchange interactions to vary from those corresponding to a bulk sample, in which these interactions produce the maximum possible hyperfine field, to possibly considerably reduced interactions for more poorly crystallized regions. In ferrihydrite, crystallinity is consistently poor. This gives Mössbauer spectra which are centered around a field corresponding to the average crystallinity. The hyperfine field distributions observed for ferrihydrite therefore are more or less symmetric, because they have no components of fields resulting from regions of bulk crystallinity. The electron micrographs of lepidocrocite, on the other hand, show the crystallinity of this mineral to vary from very poor to good (fig. 1a, b). Consequently the hyperfine field distributions shown by magnetically ordered lepidocrocite will also vary considerably (fig. 6). The hyperfine field distribution of well crystallized lepidocrocite (e.g. 22/568) includes components of bulk crystallinity, and is therefore skewed downwards from that maximum field (458 kOe). In contrast, the field distribution for the more poorly crystallized lepidocrocite (P23) contains only subordinate components from regions of bulk crystallinity, and is therefore, like those observed for ferrihydrite, more symmetric (Murad and Schwertmann, 1980). The hyperfine field of maximum absorption (c. 445 kOe) of both studied lepidocrocites is less than that of ferrihydrite at 4.2 K (470 to 500 kOe) and may, in conjunction with the somewhat narrower half widths of hyperfine field distributions (c. 20–50 kOe vs. 65–90 kOe), serve to distinguish these minerals.

Conclusions. The Néel temperature of lepidocrocite is higher than hitherto assumed, and probably lies at 77 ± 1 K. The differences between the Mössbauer spectra of the studied samples are due to superparamagnetic relaxation and other particle-size phenomena, resulting from poor crystallinity of P23 and a somewhat better crystallinity of 22/568. Because relaxation tends to produce atypical Mössbauer spectra in the vicinity of the Néel temperature, such spectra should, if they are to be specific, be taken at temperatures considerably below 77 K. Depending on crystallinity, lepidocrocite spectra show moderate to widely asymmetric distributions of magnetic hyperfine fields at 4.2 K, with a maximum field of about 460 kOe and a low quadrupole splitting of about 0.04 mm s^{-1} .

Acknowledgements. We are indebted to F. E. Wagner for placing the Mössbauer spectrometers used for the low-temperature measurements at our disposal and to L. H. Bowen for a constructive review of the manuscript. Thanks are also extended to H. Ch. Bartscherer for taking the electron micrographs, to L. H. Bowen for making the services of the North Carolina State University at Raleigh available while we were writing this paper, and to the Deutsche Forschungsgemeinschaft for financial support.

REFERENCES

- Bowen, L. H. (1979) *Mössbauer Effect Ref. Data J.* **2**, 76–94.
 Ewing, F. J. (1935) *J. Chem. Phys.* **3**, 420–4.
 Johnson, C. E. (1969) *J. Phys.* **C2**, 1996–2002.
 Kraan, A. M. van der (1973) *Phys. stat. sol.* **a18**, 215–26.
 Kündig, W., Bömmel, H., Constabaris, G., and Lindquist, R. H. (1966) *Phys. Rev.* **142**, 327–33.
 — Ando, K. J., Lindquist, R. H., and Constabaris, G. (1967) *Czech. J. Phys.* **B17**, 467–73.
 Mørup, S., Madsen, M. B., Franck, J., Villadsen, J., and Koch, C. J. W. (1983) *J. Magnetism Magnetic Mater.* **40**, 163–74.
 Murad, E. (1982a) *Neues Jahrb. Mineral. Mh.* 45–56.
 — (1982b) *Am. Mineral.* **67**, 1007–11.
 — and Schwertmann, U. (1980) *Ibid.* **65**, 1044–9.
 Schwertmann, U., and Taylor, R. M. (1972) *Clays Clay Mineral.* **20**, 151–8.
 — Schulze, D. G., and Murad, E. (1982) *Soil Sci. Soc. Am. J.* **46**, 869–75.
 Wivel, C., and Mørup, S. (1981) *J. Phys.* **E14**, 605–10.
 Yamamoto, N. (1968) *Bull. Inst. Chem. Res. Kyoto Univ.* **46**, 275–82.

[Manuscript received 9 September 1983;
 revised 9 January 1984]