

⁵⁷Fe MÖSSBAUER EFFECT STUDY OF WELL-CRYSTALLIZED GOETHITE (α -FeOOH)

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Well-crystallized, natural goethite has been investigated as a function of temperature. The saturation magnetic hyperfine field was found to be 507 kOe and the Néel temperature $T_N = (400 \pm 2)$ K. The antiferromagnetic structure is stable in external fields of up to 60 kOe and the spin direction is at right angles with respect to the EFG's principal axis. At $T/T_N < 0.5$, the reduced hyperfine field varies as T^2 and in the range $0.80 < T/T_N < 0.97$ as $T^{1/3}$. From the temperature dependence of the isomer shift, the Debye temperature was found to be 440 K from which a relative Mössbauer fraction of 0.96 against hematite was evaluated.

Goethite, α -FeOOH, has been the subject of numerous Mössbauer spectroscopic studies, especially in relation to soil characterization. It is well known /1/ that the Mössbauer spectra are characteristic for the crystallinity of the goethite. For natural samples, substitutions of other elements (e.g. Al and Mn) play a major role as well. For most natural and synthetic goethites the degree of crystallinity is low and this is reflected in the asymmetric line shape of the spectra and in the partial or complete collapse of the hyperfine structure at room temperature. Well-crystallized goethite is found in e.g. Loswithiel (Cornwall, England) and in the Harz mountains (West Germany) /2/. Samples from the former location have extensively been studied by van der Woude and Dekker /3/ and by Forsyth et al. /4/. The present paper reports ⁵⁷Fe Mössbauer effect measurements between 10 and 410 K on a sample from the Harz mountains. Using external magnetic fields, earlier conclusions with respect to the sign and the orientation of the *electric field gradient* (EFG) /3,4/ are confirmed.

X-ray powder diffraction showed that the Harz sample was pure, single-phase goethite. There is no indication, whatsoever, of line broadening due to crystal imperfections and/or small particle dimensions. Electron micrographs show particles of no particular shape, most of them with dimensions of the order of 1 μ m. Some smaller particles are present too ($\lesssim 1000$ Å) but these constitute only a minor fraction of the total mass.

Some Mössbauer spectra at relatively high temperatures are collected in Fig. 1.. They were recorded with a conventional time-mode spectrometer (for details see ref. /5/). Up to 320 K, the spectra are well described by a single sextet. The line width Γ (FWHM) is constant at 0.28 ± 0.01 mm/s for all temperatures. All spectra contain an additional, small sextet component which is due to the presence of a few percent of hematite (α -Fe₂O₃), not detected by the X-ray diffraction.

From 340 K on, a central quadrupole doublet starts to develop and the line shape of the sextet component becomes more and more asymmetric. The spectra are

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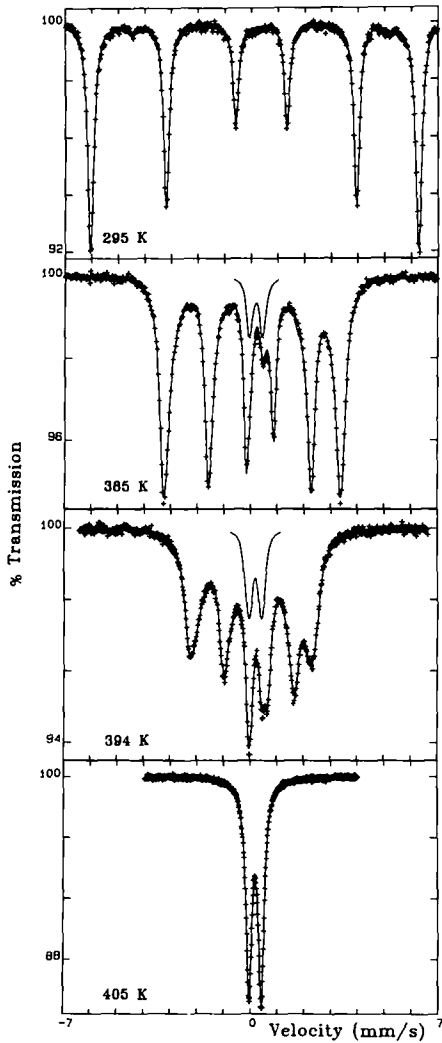


Fig. 1.: ^{57}Fe Mössbauer spectra of Harz goethite at some selected temperatures. Full lines are calculated spectra. Arrows indicate the presence of hematite.

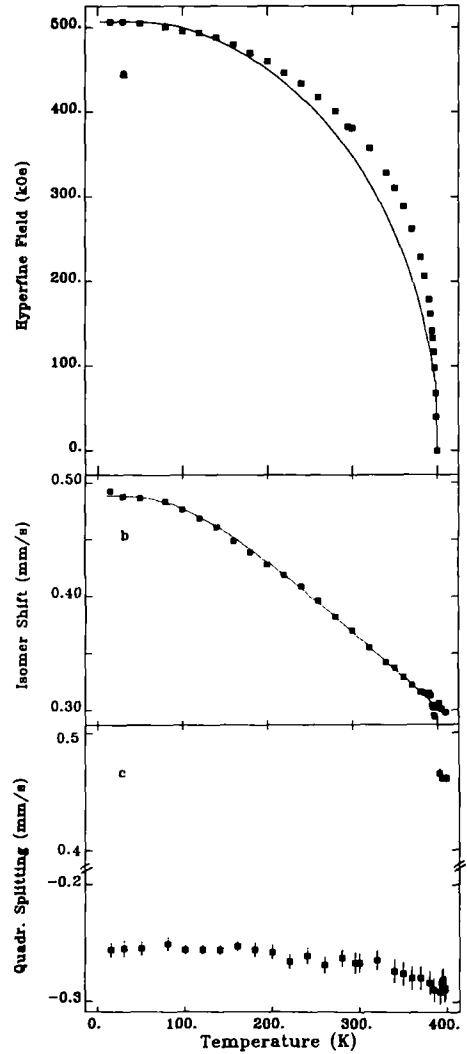


Fig. 2.: Temperature dependence of the magnetic hyperfine field (a), the isomer shift versus αFe (b) and the quadrupole splitting (c). Full lines are theoretical relations.

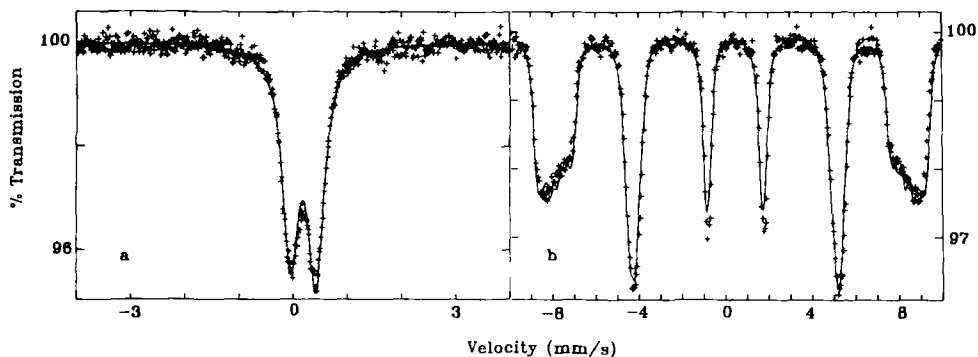


Fig. 3. : Mössbauer spectra of Harz goethite in applied magnetic fields ;
 (a) $T = 405$ K, $H_{app} = 2.4$ kOe; (b) $T = 19$ K, $H_{app} = 60$ kOe..
 Full lines are simulated spectra.

quite well reproduced by a distribution of magnetic hyperfine fields and a superimposed quadrupole splitting distribution ranging between 0.2 and 1.0 mm/s /6/. In executing the computer fits, the $\alpha\text{Fe}_2\text{O}_3$ contribution was first stripped off and the isomer shift was forced to be the same for both goethite components.

At 402, 405 and 410 K, a pure quadrupole doublet is obtained. There is a slight asymmetry of 51:49 in the peak areas which can be attributed to texture effects. The quadrupole splitting is 0.47 mm/s.

Fig.2 depicts the temperature dependence of the magnetic hyperfine field H_{hf} (field of maximum probability in the case of hyperfine field distribution fits), the isomer shift δ (versus Fe) and the quadrupole splitting $2eQ$.

The external field measurements are presented in Fig.3a en b. The first spectrum was obtained at 405 K in a field of 2.2 kOe. The doublet is more asymmetric as compared to the zero-field spectrum. The full line in Fig.3a was evaluated from the total interaction hamiltonian, using the zero-field hyperfine data at 405 K and a positive sign for the EFG. The asymmetry parameter η was taken to be zero. Fig.3b refers to $T = 19$ K and an applied field of 60 kOe. The full line represents the simulated line shape obtained with the assumption that the EFG and the spin direction make an angle of $80 \pm 10^\circ$. Again, η was taken to be zero. The agreement between the experimental and the calculated relative line intensities is not complete. It is believed, however, that the deviations are due to the same effect which causes the area ratios in the zero-field spectra to deviate from the ideal 3:2:1.

To a good approximation, the Fe^{3+} magnetic hyperfine field is proportional to the sublattice magnetization m_S . The simplest model describing the temperature variation of m_S is the Weiss molecular field theory which predicts a Brillouin curve for $m_S(T)$. The full line in Fig.2a represents such curve for spin $S = 5/2$, saturation field $H_{hf}(0) = 507$ kOe and Néel temperature $T_N = 400$ K. It is obvious that considerable discrepancies with the experimental field values exist in the range $T/T_N > 0.4$, which is consistent with the results for Loswithiel goethite /3/.

It was observed that for $T/T_N < 0.5$, the reduced hyperfine field $H_{hf}(T)/H_{hf}(0)$ varies quadratically with temperature. Such a behaviour was predicted by Kubo /7/ for a simple two-lattice antiferromagnet based on the spin-wave concept :

$$m_S(T) = 1 - 1.59 \cdot 10^{-3} k^2 T^2 / (2J_e)^2 \quad (1)$$

with J_e the inter-sublattice exchange interaction, thus calculated to be 13 K, which is a reasonable value. At higher temperatures, i.e. $0.80 < T/T_N < 0.97$, the hyperfine field was found to vary as :

$$H_{\text{hf}}(T)/H_{\text{hf}}(0) = D(1-T/T_N)^\beta \quad (2)$$

From least-squares fitting, the quantities D and β were found to be 1.23 and 0.335 respectively. These values are in good agreement with the theoretical ones ($D=1.22$ and $\beta=0.323$) calculated by Callen and Callen /8/ from the two-spin cluster approximation for ferromagnets with nearest and next-nearest neighbour interactions.

The presence of a central doublet at temperatures close to T_N , indicates that the magnetic transition does not proceed uniformly for all goethite crystallites. The nature of the doublet, i.e. paramagnetic or superparamagnetic could not be determined with the available equipment. The authors of refs. /3/ and /4/ do not mention the development of a central doublet. This could mean that the magnetic transition is much more uniform in Loswithiel goethite. It could be, however, that the observation of the doublet was missed because it is obvious for $0.960 < T/T_N < 0.985$ only. At lower temperatures, the doublet contribution is only a few percent and at higher temperatures, it is no longer resolved from the innermost lines of the magnetic component. Spectra recorded on the Harz goethite at 395, 396, 397 and 398 K are indeed very similar to those plotted in Fig.4 of ref. /3/.

The numerical evaluation of the spectrum plotted in Fig.3b and the sudden drop of the quadrupole interaction at T_N to a negative value with a magnitude of nearly one half of the high-temperature value, both indicate that the principal axis of the EFG and the direction of H_{hf} are perpendicular. This finding is in agreement with the conclusion of van der Woude and Dekker /3/ based on point-charge calculations of the EFG tensor. According to Forsyth et al. /4/, the spins are aligned parallel to the c -axis and the major EFG axis lies in the ab plane.

The temperature dependence of the isomer shift δ is due to the second-order Doppler shift and can be calculated using the Debye approximation of the lattice vibrations /9/ thus containing the Debye temperature Θ_D as an adjustable parameter. Once Θ_D is known, the Mössbauer fraction f can be evaluated. The full line in Fig.2b is the calculated temperature variation with $\Theta_D = 440$ K. This further yields $f = 0.803$ at 300 K, or, more significant, $f_H/f_G = 1.04$ in which H and G refer to bulk hematite and Harz goethite respectively. The fraction f_H has been determined in a previous paper /10/. In order to check the significance of the relative Mössbauer fraction, a spectrum was recorded for a reference hematite/goethite mixture with equal thicknesses (2.5 mg Fe/cm^2) for both components. From the relative absorption areas, a ratio f_H/f_G of 1.08 ± 0.03 was calculated which is in reasonable agreement with the former value.

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