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Mössbauer spectra of ferrihydrite: superferromagnetic interactions and anisotropy local energy

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Abstract. The Mössbauer spectra of a sample of synthetic ferrihydrite have been investigated in the 26–220 K temperature range in order to identify the mechanism giving rise to the relaxation times. The results show that the temperature dependence of the relaxation times is in accordance with the Vogel–Fulcher law. This indicates that the magnetic interaction between the crystallites is significant. From the temperature dependence of the mean magnetic field under T_B we also argue for a strong correlation between the spatial orientations of neighbouring clusters.

1. Introduction

In the past, ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$) has been the subject of a great deal of theoretical and experimental work. The existence of relaxation phenomena is obvious at intermediate temperatures; however, their origin has not yet been identified. It is tacitly assumed, from the analogy of the behaviour of similar compounds, that the kind of mechanism giving rise to relaxation is superparamagnetic [1–3]. In this paper a systematic study of the modifications of the Mössbauer spectrum as a function of the temperature T is presented. Relaxation times above the blocking temperature T_B and the local magnetic fields below T_B have been measured as a function of the temperature T. It turns out, in contrast with what was previously assumed, that the relaxation mechanism comes from superferromagnetic interactions.

2. Experimental details

The ferrihydrite sample was prepared by means of the method described in [1]. Moreover, in order to remove the interstitial water, the sample was subjected to thermal treatment. For the purpose the sample was maintained for some days under vacuum conditions at a temperature of 350 K. This procedure proved to be necessary in order to obtain reproducible spectra. Similar procedures have been reported by other workers in studies of goethite [4] and of ultrafine ferrite particles [5].

A sample was ultrasonically dispersed in water and TEM micrographs were obtained using a Philips CM10 microscope operating at 80 kV. The electron micrographs exhibited

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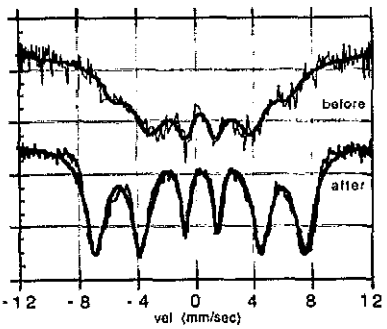

Figure 1. Spectra for $T = 26$ K recorded before and after the thermal treatment. So that the spectra could be compared easily, different vertical scales were used.

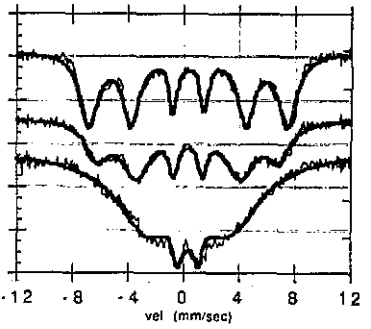

Figure 2. Spectra under T_B for $T = 26$, 40 and 50 K from top to bottom, respectively. So that the spectra could be compared easily, different vertical scales were used.

close-packed particles of approximately 50–70 Å size, forming spherical aggregates of approximately 200–300 Å size. Our micrographs are similar to figure 3 in [6].

The sample was cooled using a closed-cycle refrigerator. The Mössbauer spectra were obtained using a ^{57}Co–Rh source. The linewidth enlargement due to the spurious vibrations was negligible (about 0.01 mm s^{-1}) [7] but, on the other hand, the lowest temperature obtained was 26 K.

Figure 1 shows the spectra for $T = 26$ K recorded before and after the thermal treatment. At low temperatures the Mössbauer spectrum of ferrihydrite consists of a magnetic sextet with a zero electric quadrupole interaction. The magnetic hyperfine field value agrees with those reported in the literature [2, 8]. At room temperature the Mössbauer spectrum is a doublet. Figures 2 and 3 show the variation in the Mössbauer spectrum as a function of the temperature T. By increasing the temperature the magnetic field progressively disappears. The transition temperature T_B at which the six-line pattern collapses into a doublet is the so-called 'blocking temperature'.

The magnetic spectra are rather broad, thus indicating a distribution of magnetic fields. From the width of the 26 K spectrum external lines ($\Gamma = 1.4$ mm s^{-1}), one can roughly estimate the magnetic field average relative variation $\Delta H/H$ at low temperatures. It turns out that $\Delta H/H \simeq 20\%$.

In order to take into account the slow-relaxation effects below T_B the low-temperature spectra were fitted by means of a Blume–Tjon sextet. The spectra recorded at $T = 55$ and 60 K were ruled out because they were too close to T_B. In this case a large range of relaxation times is present; moreover the shape of the spectrum is strongly dependent on the relaxation time value.

For $T > T_B$ the linewidth of the quadrupolar doublet decreases by increasing T, whereas the quadrupole splitting remains almost constant (about 0.70–0.72 mm s^{-1}). Since the quadrupolar interaction is apparently absent in the low-temperature spectra, we conclude that the directions of the magnetic field and of the electric field gradient (EFG) tensor principal axis form an angle near to 54° [2].

This value corresponds to the angle formed, in a cubic structure, by a C_3 axis and a C_4 axis. Since the local symmetry at the iron site is nearly cubic, with a small trigonal distortion [9, 10], the principal axis of the EFG tensor must then coincide with a C_3 axis and the magnetic field is along a C_4 axis (figure 4). Obviously there are six possible equivalent directions for the magnetic field.

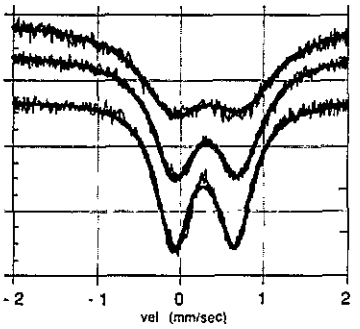

Figure 3. Spectra above T_B for T = 65, 75 and 160 K from top to bottom, respectively. So that the spectra could be compared easily, different vertical scales were used.

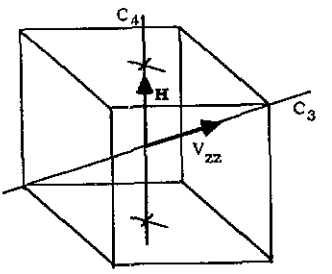

Figure 4. EFG tensor principal axis V_{zz} and one of the six possible H directions. The C_3 and C_4 axes are also indicated.

3. Results and discussion for $T > T_B$

The relaxation time and its physical mechanism can easily be shown from the analysis of the spectra for $T > T_B$. The linewidth and the intensities of the two lines of the doublet are essentially equal; this corresponds to isotropic relaxation. This relaxation takes place between the six possible magnetic field orientations. In contrast with what was found in other similar compounds, in the present case, below T_B, the spectra are not a superposition of a relaxed structure and a magnetic structure. This suggests that the physical mechanism which blocks the grain magnetic moments is superferromagnetic. Other facts confirm this kind of mechanism [11]:

(i) the strong variation, after the thermal treatment, of the shape of the spectra below T_B (figure 1) and

(ii) the increase in the blocking temperature (about 4 K) after the thermal treatment.

For $T > T_B$, one is in the fast-relaxation limit, so that the relaxation time τ can be easily evaluated [12].

Figure 5 shows a comparison between the obtained τ-values and the theoretical values estimated by means of the Vogel–Fulcher law [13]:

$$\tau = \tau_0 \exp[T_1/(T - T_B)]$$

where τ_0 and T_1 denote two constants. From a least-squares fitting, one finds that $\tau_0 = 1.22(\pm 0.05) \times 10^{-10}$ s, $T_1 = 13(\pm 2)$ K and $T_B = 54(\pm 1)$ K.

T_1 depends on the local anisotropy energy T_k ($T_1 \simeq T_k$ in the weak-coupling approximation and $T_1 \simeq T_k/2$ in the strong-coupling case), whereas T_B is the ratio of the square of the superferromagnetic interaction to the local interaction [13].

The fact that we found $T_B > T_1$ is consistent with the superferromagnetic relaxation. Starting from the theory in [13] and from the experimental values of T_B and T_1, one can obtain the following values for the superferromagnetic and the local anisotropic constants T_{SF} and T_k. They are $T_{SF} = 37$ K and $T_k = 26$ K.

4. Results and discussion for $T < T_B$

The dependence of the mean magnetic hyperfine field H as a function of the temperature was deduced from the spectra for $T < T_B$.

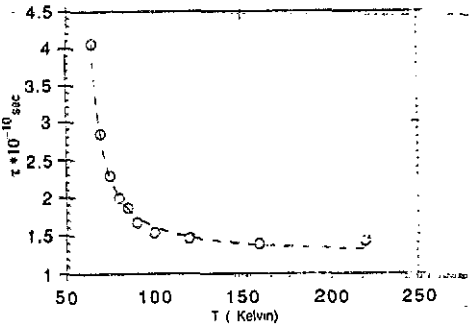

Figure 5. Relaxation time τ versus temperature for $T > T_B$.

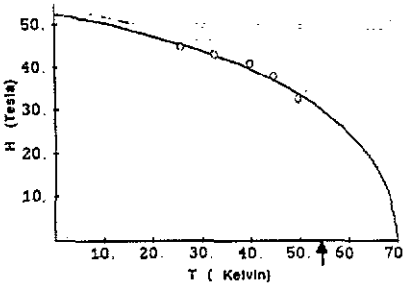

Figure 6. Best fit of the magnetic field values by means of the Weiss theory. The predicted value for T_B is 70 K. The arrow indicates the experimental T_B-value.

We point out that the presence of the magnetic splitting in the spectra from 26 to 54 K is due to the superferromagnetic interaction. Since $T_1 = 13$ K, without a strong interaction between neighbouring grains, the 26 K spectrum should also consist of a doublet.

Figure 6 shows a comparison between the experimental values of the magnetic field H and the theoretical values deduced from the Weiss theory. In contrast with the case of goethite [14], in the present case such a theory is completely inadequate. Not only is the fitting poor but the predicted value for T_B is too high. In our case for low temperatures the magnetic field decreases very slowly with increasing T, and then near T_B it undergoes a sudden collapse. In contrast a classical theory predicts that, before collapsing, the magnetic field decreases more quickly.

This means that the excitation energies of the cluster magnetic levels are not small with respect to the thermal energy kT_B. The observed behaviour therefore suggests the importance of quantum effects. The electron magnetic moment of the cell can align itself along six directions, corresponding to the magnetic field orientations at the iron nucleus. In the case of a single-domain particle the resultant magnetic moment can therefore be oriented along the same six directions. Hence we have six magnetic energy levels. Their energies depend obviously on the orientation of the cluster with respect to the magnetic field due to the neighbouring clusters.

Let us consider the two extreme situations in which a C_4 or a C_3 axis is parallel to the field. The magnetization of the cluster and the hyperfine field will depend on these orientations. Taking into account the level schemes for the two cases the following expressions for the magnetic field value $H(T)$ as a function of the temperature T are

$$[\exp(xf/T) - \exp(-xf/T)]/[\exp(xf/T) + \exp(-xf/T) + 4] = f$$

$$\cos(\theta)\tanh[\cos(\theta)(xf/T)] = f$$

where $f = H(T)/H(0)$, θ is the angle between the C_4 axis and the C_3 axis, and x and $H(0)$ are fitting parameters.

The energy levels of the cluster leading to the observed behaviour of the magnetic hyperfine field were derived by means of a fitting procedure. Figures 7 and 8 show the results obtained by a least-squares minimization procedure, assuming that the local magnetic field is parallel to a C_4 or a C_3 cluster axis respectively. We point out that, in order to fit the experimental points, we used two different vertical scale factors for the

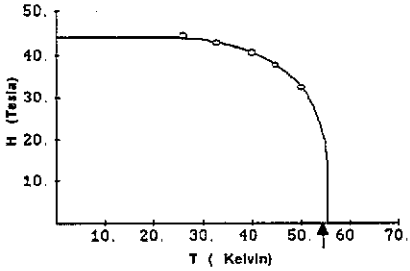

Figure 7. Best fit of the magnetic field values assuming that a C_4 axis is parallel to the local external field. The predicted T_B-value is very close to the experimental value, which is indicated by the arrow.

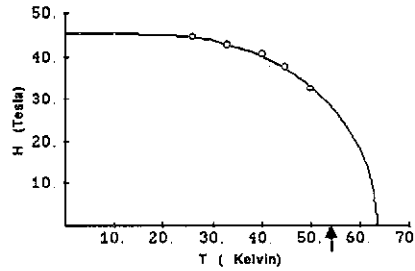

Figure 8. Best fit of the magnetic field values assuming that a C_3 axis is parallel to the local external field. The predicted value for T_B is 64 K. The arrow indicates the experimental T_B-value.

two cases. In fact in the second case the magnetic field is cos(54) = 0.58 times that in the first case.

Therefore, if the clusters were differently oriented with respect to the local field, the 26 K spectrum should exhibit a wide distribution (1–0.58) of hyperfine fields not observed after the thermal treatment.

We obtained the best result by supposing that the C_4 axis was parallel to the external local field. Moreover in this case the predicted T_B-value is close to the experimental value. Hence we argue for a strong correlation between the spatial cluster orientations so that there is a high probability that a crystallite C_4 axis is parallel to the external local field. This is not surprising because such a configuration minimizes the magnetic energy of the cluster in the local magnetic field.

Acknowledgment

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