



Mössbauer Measurements on Spinel-structure Iron Oxide Nanoparticles

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Mössbauer spectra were measured for ⁵⁷Fe in two samples of iron oxide nanoparticles made from iron oleate. One sample was prepared in paste form with a particle diameter of 15 ± 1 nm, a superparamagnetic blocking temperature $T_B \approx 300$ K, and a deduced magnetic anisotropy of $K \approx 0.52 \times 10^4$ J/m³. The other was prepared as a powder with a particle size of 7.5 ± 1.0 nm and $T_B \approx 120$ K. At low temperatures their spectra were identical but unlike that of bulk Fe₃O₄. Both samples were concluded to have oxidized from Fe₃O₄ to γ -Fe₂O₃. The powder sample also contained about 30% of α -Fe₂O₃ impurity which was not superparamagnetic but had a reduced Morin temperature.

1. Introduction

Magnetic nanoparticles are single-domain and exhibit superparamagnetism and decreased magnetization in small applied fields. In superparamagnets the magnetic moments of the particles fluctuate rapidly between the Curie temperature T_C and a temperature T_B known as the blocking temperature. This produces a reduced magnetization and (in the Mössbauer spectrum) a broadened hyperfine spectrum. Below T_B the usual magnetic moment and hyperfine splitting are observed.

Since there is a large fraction of atoms on the surface of small particles, there may be surface effects, including oxidation. This can lead to a difference in properties of surface atoms in comparison to those deep in the particle. Mössbauer spectroscopy affords a method of studying these features including detecting the oxidation.

In this paper Mössbauer measurements on nanoparticles of superparamagnetic iron oxide will be described. Iron oxide nanoparticles find many applications including to biomedicine [1] and information storage. Many previous studies of these materials have been made (e.g. [2-4]) and it is clear that their properties may depend on the method of preparation as well as their size. Hence two methods were used for comparison.

2. Sample preparation

Nanoparticles of ferrimagnetic iron oxide were synthesized through the thermal decomposition [5] of an iron oleate precursor in the presence of oleic acid. This method produces good size control and avoids use of more toxic chemicals. First, the oleate precursor was produced by mixing 2.2 g of FeCl₃.6H₂O (Sigma Aldrich) and 7.3 g of sodium oleate (Sigma Aldrich) with 16 mL of ethanol (Pharmco-AAPER), 28 mL of hexane (Fisher), and 12mL of deionized water. Thereafter, the mixture was heated to 70 °C and maintained at this temperature for four hours. Next, the nanoparticles were synthesized by thermal

decomposition, initially at 220 °C and subsequently at 290 °C, of a solution containing 1.6 mmol of iron oleate and 0.8 mmol of oleic acid in 10 mL of 1-octadecene (Sigma Aldrich). The solution was then mixed and degassed at 100 °C for 30 min, after which it was heated at a rate of 3 °C/min to 320 °C. Finally, the solution was refluxed for 45 min. The resulting nanoparticles were precipitated from the synthesis solution by centrifugation and resuspended in ethanol until needed in the experiments.

Two different Mössbauer samples resulted from extracting the nanoparticles from the suspension. The *paste* sample was produced by heating the suspension to approximately 70 °C, and allowing it to cool under atmospheric conditions. The resulting nanoparticles had a diameter of 15.0 ± 1.0 nm and the concentrated paste was transferred to the sample holders for experiment or to a vial for storage. On the other hand the *powder* sample was produced through freeze drying under vacuum and the resulting nanoparticles had a diameter of 7.5 ± 1.0 nm. TEM images of the resulting nanoparticles are shown in Fig. 1.

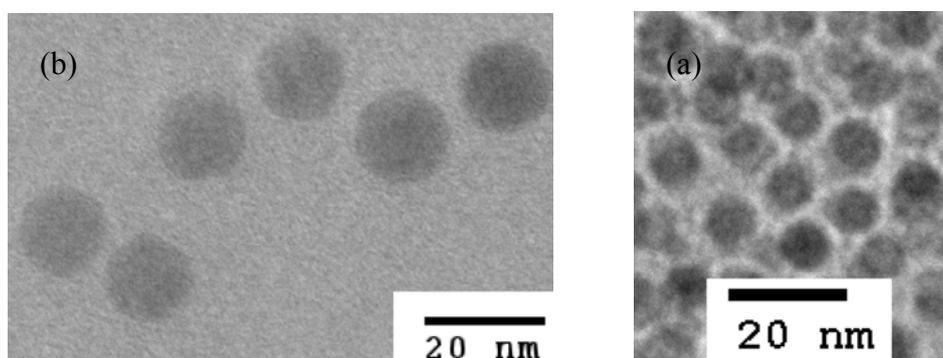


Fig. 1. TEM images of (a) the paste sample and (b) the powder sample.

3. Results

3.1 Paste sample

Fig. 2 shows Mössbauer spectra of the paste sample of the nanoparticles at a series of temperatures between 220 and 6 K. The spectrum is broad at the higher temperatures and becomes a well-resolved 6-line pattern with line widths decreasing as the sample is cooled. At 6 K, the saturation hyperfine field is 515 kG and the line width of the outer lines is 0.63 mm/s.

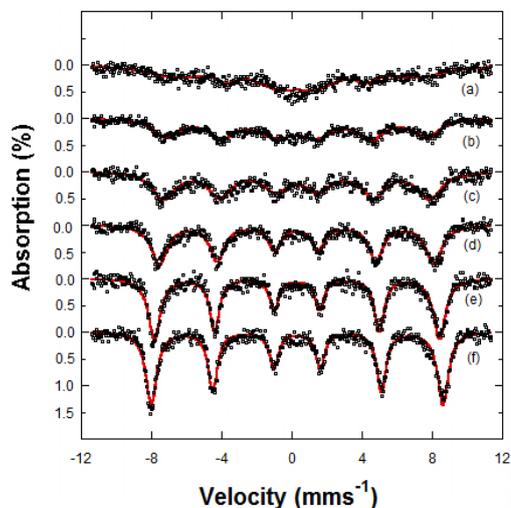


Fig. 2 Mössbauer spectra of the paste sample at (a) 220 K (b) 150 K (c) 128 K (d) 90 K (e) 40 K (f) 6 K. The solid lines are fits to each spectrum with six Lorentzian lines.

The isomer shift is constant at 0.41 mm/s which falls in the range of values expected for Fe³⁺ in octahedral coordination. The variation with temperature of the fitted mean hyperfine field B_{hf} and linewidth Γ of the outer lines is given in Table I. Due to relaxation effects, the line shapes are strictly not Lorentzian at higher temperatures but the fitted line width values are included as a useful indication of the extent of the spectral broadening. From Fig. 2, the spectrum evidently collapses to a non-magnetic doublet at a temperature well above 220 K. Spectra recorded at temperatures higher than those shown in Fig. 2 show that T_B is close to 300 K.

Table 1. Fitted Mössbauer data for the paste sample

T(K)	B_{hf} (kG)	Γ (mm/s)
270	-	-
220	410	3.81
150	464	1.72
128	469	1.57
90	485	0.95
40	503	0.81
6	515	0.63

3.2 Powder sample

Mössbauer spectra recorded for the powder sample of the nanoparticles are shown in Fig. 3 for a series of temperatures between 260 and 4 K. The results at the lowest temperature are similar to those of the paste sample in that there is a 6-line magnetic Fe³⁺ spectrum with broad lines ($\Gamma = 0.6$ mm/s) and a hyperfine field of about 515 kG. However, there is a second 6-line pattern with 30% of the intensity of the main spectrum and almost overlapping it. This

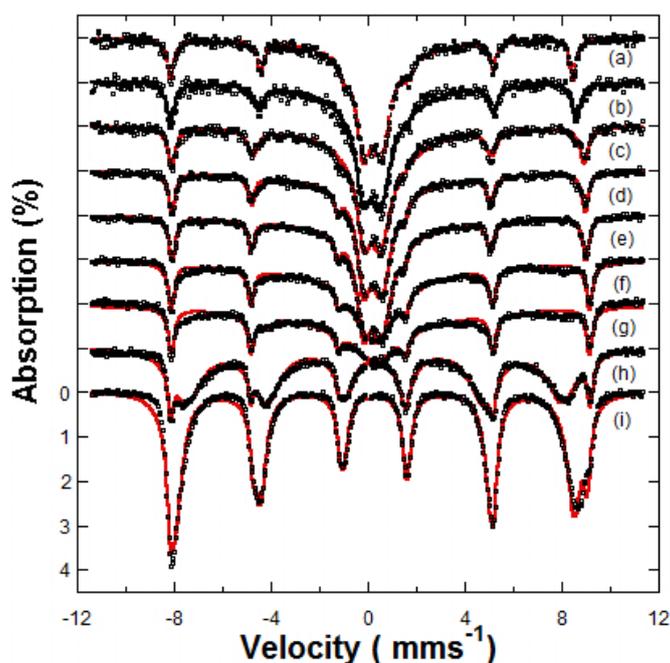


Fig. 3. Mössbauer spectra of the powder sample at (a) 260 K (b) 230 K (c) 220 K (d) 210 K (e) 200 K (f) 100 K (g) 80 K (h) 40 K (i) 4 K



additional spectrum has a similar hyperfine field but narrower lines ($\Gamma = 0.3$ mm/s) and, from its quadrupole splitting, can be identified as arising from α -Fe₂O₃.

The main 6-line spectrum shows a decrease in hyperfine splitting with increasing temperature, so that the two spectra become easily distinguished from each other. In addition, the lines of the main spectrum become broadened in a way similar to those in the paste sample except that they collapse to a non-magnetic doublet just above 100 K. Hence T_B is estimated to be about 120 K. This is substantially less than the value of T_B estimated for the paste sample, in accord with the smaller size (7.5 nm compared with 15 nm) of the powder nanoparticles.

The hyperfine field of the α -Fe₂O₃ sub-spectrum is almost independent of temperature. Furthermore, its quadrupole coupling changes sign between 220 and 230 K due to the Morin transition, which is a characteristic of α -Fe₂O₃. In bulk α -Fe₂O₃ the Morin transition occurs at 260 K.

4. Estimation of the anisotropy constant for the paste nanoparticles

Below the blocking temperature, T_B , the superparamagnetic fluctuations (i.e. fluctuations of the magnetic moments of the single-domain particles) are slow but the magnetization within each particle fluctuates rapidly about the easy axis (collective magnetic fluctuations). According to a simplified model of uniaxial anisotropy, the energy is given by

$$E(\theta) = KV\sin^2\theta \quad (1)$$

where θ is the angle between the magnetization vector and the easy axis, K is the anisotropy constant and V is the particle volume. In the context of this model, Mørup [4] has shown that the hyperfine field below T_B varies approximately as

$$B_{\text{hf}}/B_{\text{hf}}^0 = 1 - kT/2KV \quad (2)$$

where B_{hf}^0 is the saturated value of B_{hf} at $T = 0$ K. Hence KV can be determined and, if the nanoparticle volume is known, the anisotropic constant can be estimated.

In Fig. 4, the hyperfine field for the paste sample is plotted as a function of temperature using the data from Table 1. A least-squares fit shows that $B_{\text{hf}}^0 = 517$ kG and the slope

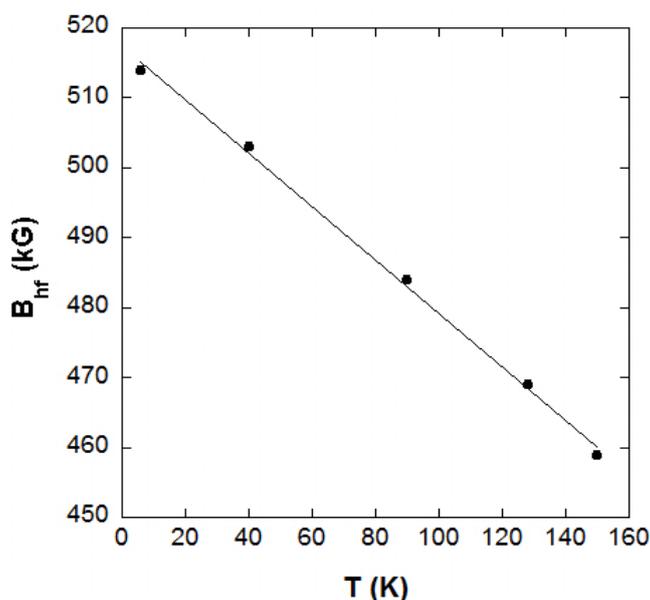


Fig. 4. Temperature dependence, below T_B , of the fitted mean hyperfine field for the paste sample (taken from Table 1).



$\Delta(B_{\text{hf}}/B_{\text{hf}}^0)/\Delta T = -7.4 \times 10^{-4} \text{ K}^{-1}$. Hence KV for the paste particles is $0.92 \times 10^{-20} \text{ J}$. Taking the diameter of the particles (assumed spherical) to be 15 nm, it is found that $K \approx 0.52 \times 10^4 \text{ J/m}^3$.

In principle, a similar approach could be applied to the powder sample. However, the detailed analysis will depend on assumptions about the $\alpha\text{-Fe}_2\text{O}_3$, which is presumably on the nanoparticle surface.

5. Discussion

The spectra are different from those previously found [3] for nanoparticles of Fe_3O_4 although the hyperfine field values at low temperatures are similar. We observe only a single 6-line pattern, whereas Fe_3O_4 is a superposition of two sub-spectra, one arising from Fe^{2+} ions and the other with a higher intensity arising from Fe^{3+} ions. Also there is no sign of the Verwey transition. Hence we conclude that the nanoparticles are not comprised of Fe_3O_4 .

A likely candidate is $\gamma\text{-Fe}_2\text{O}_3$, nanoparticles of which have been studied by Predoi *et al* [6] and Rebbouh *et al* [7] whose spectra are similar to ours. Predoi *et al* deduce an anisotropy constant of $K = 2.1 \times 10^4 \text{ J/m}^3$. Further evidence comes from the work of Sousa *et al* [8] on $\text{NiFe}_2\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ core/shell nanoparticles for which they find $K = 2.5 \times 10^4 \text{ J/m}^3$. It may be noted that the anisotropy for bulk Fe_3O_4 (below the Verwey transition) is $2 \times 10^5 \text{ J/m}^3$, which is an order of magnitude greater than for $\gamma\text{-Fe}_2\text{O}_3$.

The blocking temperature T_B is not a transition temperature in the thermodynamic sense, such as is the case for the Curie temperature T_C . It is the temperature where the superparamagnetic fluctuation time becomes comparable with the time of a measurement. As such it depends on how it is measured. In addition, as there is a spread in particle sizes there will be a spread in blocking temperatures which will contribute to the Mössbauer linewidth. A further complication is that there are differing definitions of the blocking temperature; some groups define it as the temperature below which the fluctuations cease and this is different from the temperature for which the magnetic and non-magnetic contributions to the Mössbauer spectrum are equal.

According to Néel the characteristic time τ for the fluctuations obeys

$$\tau = \tau_0 \exp(KV/kT) \quad (3)$$

where τ_0 is about 10^{-9} s . Using the first definition of the blocking time, which sets the time of measurement to be equal to τ at $T = T_B$, this expression can be used to estimate T_B . For a magnetic susceptibility measurement, τ is usually taken to be 100 s, and Equ. (3) then gives $T_B = KV/k \ln 10^{11} = 0.04KV/k$. On the other hand for a Mössbauer measurement τ is considerably shorter, perhaps $\sim 10^{-7} \text{ s}$ (the lifetime of the 14.4 excited state of ^{57}Fe) and $T_B = KV/k \ln 100 = 0.22KV/k$. Note there is a factor of 5 between the values of T_B derived from these different types of measurements. Using the value of $KV = 0.92 \times 10^{-20} \text{ J}$ estimated in section 4, the latter expression gives $T_B \approx 150 \text{ K}$ for our paste sample. The order of magnitude agreement with the value of $T_B \approx 300 \text{ K}$ suggested by the Mössbauer spectra (as discussed in section 3.1) must be considered fortuitous in view of the crudeness of the model assumed.

6. Conclusions

We conclude from the Mössbauer spectra that both samples have oxidized to $\gamma\text{-Fe}_2\text{O}_3$. Because a large fraction of the atoms in nanoparticles are on the surface, they are extremely vulnerable to oxidation. Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ have the same spinel crystal structure so it is difficult to distinguish between them by x-ray diffraction. Recent magnetization and Mössbauer measurements [9] on Fe_3O_4 nanoparticles report similar spectra and anisotropy constants ($K = 2.4 \times 10^4 \text{ J/m}^3$) and we suggest that their samples may also have become



oxidized to γ -Fe₂O₃. In addition, our powder sample has further been partially oxidized to α -Fe₂O₃.

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