Line Narrowing in Mössbauer Spectra of Superparamagnetic Fe₃O₄ Nanoparticles

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Abstract. Nanoparticles of magnetic crystals below a critical size are single domain and exhibit superparamagnetism. If there are N atoms or molecules with magnetic moment μ in each particle, the magnetic moment of the particle is Nμ. At high temperatures the thermal fluctuations of the magnetic moments give an ensemble average moment of zero and the Mössbauer spectrum is a single line. As the temperature, T, is lowered the fluctuations slow down and the sample acquires a magnetization and the Mössbauer line broadens and eventually shows magnetic hyperfine splitting. We have observed ^{57}Fe line broadening in nanoparticles of ferrimagnetic Fe₃O₄ with diameters of 5.3 and 10.6 nm. The results have been analyzed using the motional narrowing equation familiar in nuclear magnetic resonance to determine the superparamagnetic fluctuation time and magnetic anisotropy.

1. Introduction

Nanoparticles of ferrimagnetic iron oxide Fe₃O₄ have applications in medicine and in information technology. They are potential contrast agents in Magnetic Resonance Imaging (MRI), and in targeting and destroying cancer cells. The sharpness of an MRI image is determined by the proton (usually) spin relaxation times which can be decreased by interactions with electronic magnetic moments. Currently this is achieved by injecting gadolinium compounds, since gadolinium atoms have a large magnetic moment of 7 μ_B but magnetic nanoparticles can have magnetic moments exceeding 10^4 μ_B so are potentially more powerful. Targeting of diseased organs may be achieved either chemically (with specific molecules) or physically (with magnets) and destruction of cells is done as by heating in an rf field (hypothermia). In this paper measurements of the Mössbauer spectra of Fe₃O₄ nanoparticles of different sizes and at varying temperatures are described and used to study their magnetic properties. Mössbauer spectra have a special value in characterizing these

materials since Fe_3O_4 readily oxidizes to γ- Fe_2O_3 and shows a different spectrum but as it has the same crystal structure it cannot easily distinguished by x-ray diffraction.

Small particles of magnetic crystals below a critical size are single domain and exhibit superparamagnetism. The magnetic moment of each particle is $N\mu$ where there are N atoms with magnetic moment μ. According to Néel's theory [1] of superparamagnetism, the fluctuation time τ of particles of volume V and magnetic anisotropy K is

$$\tau = \tau_0 \exp\left(\frac{KV}{kT}\right) \tag{1}$$

where τ_0 is a characteristic time usually estimated to be between 10^{-9} and 10^{-10} s.

At high temperatures the fluctuations are fast and the macroscopic magnetic moment averages to zero and the hyperfine field measured by the Mössbauer spectrum is also zero giving a single line. As the temperature is lowered the fluctuations slow down and the line becomes broadened. Eventually at low temperatures the fluctuations are blocked and a fully split hyperfine pattern is observed. The temperature at which this happens is called the blocking temperature T_B.

This line broadening with decreasing temperature is a similar phenomenon to the motional narrowing observed in nuclear magnetic resonance (NMR) for increasing temperature. Borrowing the notation from NMR [2] the linewidth, Γ, is broadened approximately by an amount

$$\Delta\Gamma = \omega^2\tau, \tag{2}$$

where ω is the hyperfine splitting expressed as an angular frequency. This expression has the advantage of simplicity and transparency and is valid for $\omega\tau << 1$. Motional narrowing has long been studied in NMR [2] and is discussed in detail in Chapter X of Abragam's book [3] and has been applied to Mössbauer spectra by Blume and Tjon [4].

In this paper we use Mössbauer spectroscopy to characterize Fe_3O_4 nanoparticles and measure their magnetic anisotropy.

2. Experimental details
We have measured the Mössbauer spectra of ^{57}Fe in two samples of nanoparticles of Fe_3O_4 between 6 K and 300 K. The samples were prepared from a magnetite colloid and passivated by adsorbed diethylene glycol. TEM images showed that their diameters were 10.6 and 5.3 nm. The Mössbauer spectrometer was manufactured by SEECO, Edina, MN and low temperatures were obtained with a cryogen-free continuous-flow cryostat (Janis/SEECO). The measurements were made in the region of their superparamagnetic blocking temperatures T_B, i.e., where the line becomes broadened.

3. Results
The spectra show a single line at room temperature. As the temperature is lowered the line broadens and this becomes further broadened at lower temperatures and eventually shows magnetic hyperfine splitting. In general the results are complicated and the spectra are difficult to fit but they become considerably simpler in the extreme cases of high and low temperatures. Figures 1(a) and 1(b) show Mössbauer spectra of the 10.6 nm and 5.3 nm particles, respectively, at temperatures in the region of T_B. Note that for the smaller (5.3 nm) particles the transition takes place at a lower temperature (Figure 1(b)) as expected from Equation (1).

In contrast with the usual way of plotting with descending temperature from top to bottom, the spectra are plotted with temperatures in ascending order so as to emphasize the motional narrowing. At the lowest temperatures, resolved hyperfine splitting into six lines is evident, even though the lines are broad. With increasing temperature the lines coalesce into a single broad line which narrows with further increase in temperature.

4. Analysis and interpretation

The single-line spectra were fitted to a Lorentzian profile to yield values for the linewidth Γ. The broadening is $\Delta\Gamma = \Gamma - \Gamma_0$ where Γ_0 is the linewidth of 0.3 mms^{-1} observed at room temperature. There is an instrumental increase over the natural lifetime value of 0.21 mms^{-1}. The fluctuation times may be derived from Equation (2). ω is taken as the full hyperfine in. eraction which gives a total splitting of about 16 mms^{-1} in the Mössbauer spectra, corresponding to a magnetic field of about 50 T and a value $\omega = 1.105 \times 10^{-9}$ rad/s. The resulting fluctuation times are given in Table 1. Since $\omega\tau \sim 0.3$, the approximation indicated in Equ. (2) is valid.
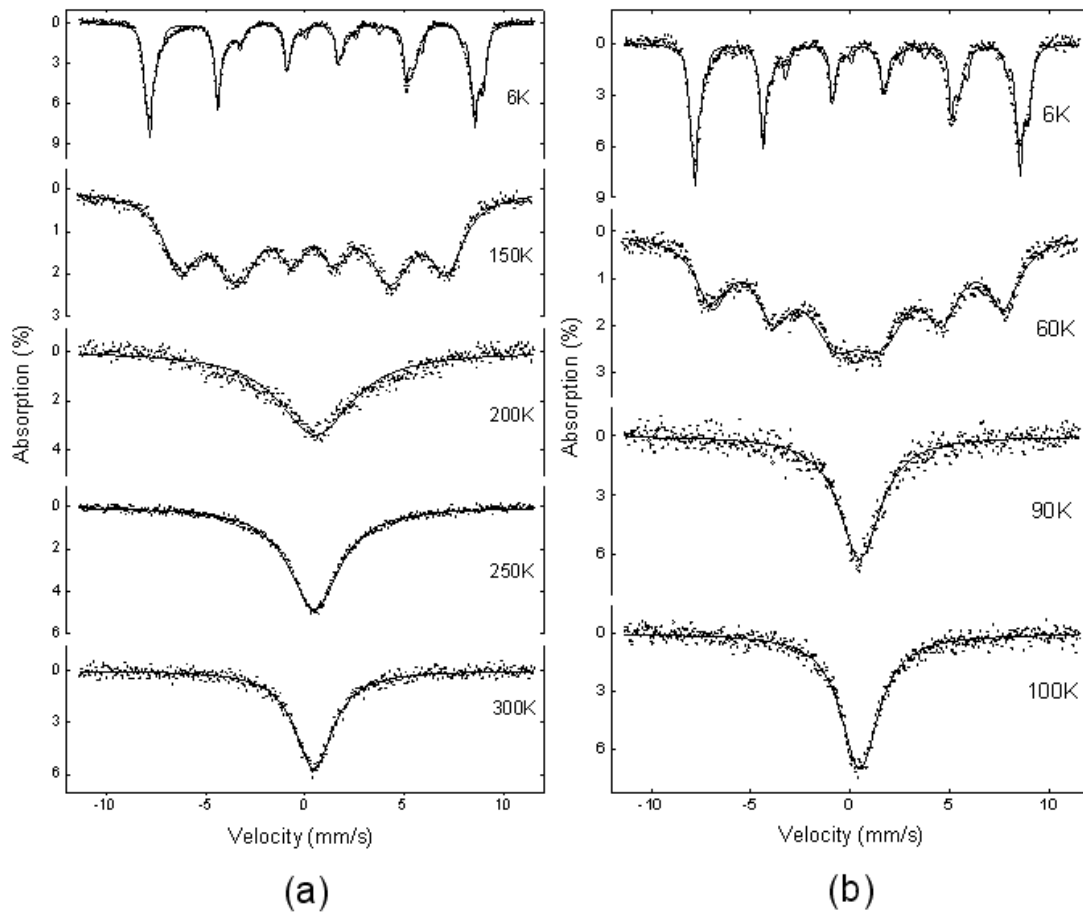
Figure 1. ^{57}Fe Mössbauer spectra of Fe$_3$O$_4$ at temperatures in the region of the blocking temperatures T$_B$ for (a) 10.6 nm and (b) 5.3 nm, particles.

**Table 1.** Nanoparticle fluctuation times.

Particle size (nm)	Temperature (K)	Linewidth Γ (mms^{-1})	fluctuation time τ (s)
10.6	200	6.55	3.35 x 10^{-10}
	250	3.12	1.67 x 10^{-10}
	300	2.37	1.11 x 10^{-10}
5.3	90	2.57	1.23 x 10^{-10}
	100	2.52	1.10 x 10^{-10}

5. Superparamagnetism

From Equation (1) it follows that

$$ln\,\tau = \frac{KV}{kT} + \ln\tau_0 \tag{3}$$

Hence a plot of $ln\,\tau$ vs. $1/T$ yields a straight line with slope KV/k and intercept $ln\,\tau_0$. From the value of KV the anisotropy can be deduced knowing the particle volume. Such a plot is shown in Figure 2 and the values of K are given in Table 2.
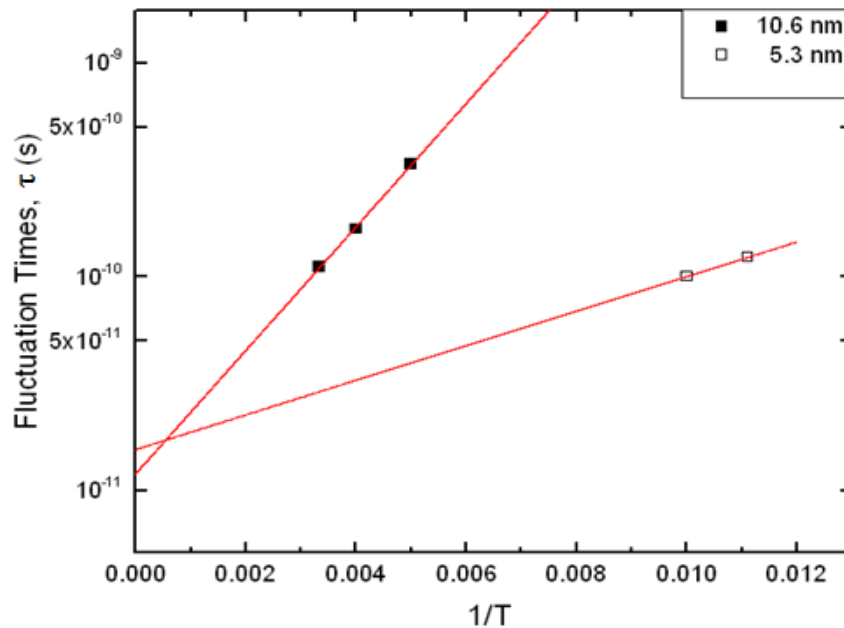
Figure 2.Plot of $ln\,\tau$ vs. $1/T$ for 10.6 nm (■) and 5.3 nm (□) particles.

Table 2. Magnetic anisotropy values.

Particle size (nm)	KV/k (K)	KV (J)	K (Jm^{-3})
10.6	665	9.18 x 10^{-21}	1.47 x 10^4
5.3	186	2.57 x 10^{-21}	3.30 x 10^4

Values of *K* have been previously determined for the same specimens from observation of collective magnetic excitations obtained from low temperature Mössbauer spectra [5]. Their values are 2.30 x 10^4 Jm^{-3} (10.6 nm) and 7.77 x 10^4 Jm^{-3} (5.3 nm). These are considerably larger (about double) than those which were measured at higher temperature. From ferromagnetic resonance measurements Bickford [6] also finds an increase in *K* as the temperature is lowered. The discrepancy probably partly arises from the simplifying assumptions of the fluctuation model we have used. It has been assumed that all the unresolved hyperfine transitions have the same linewidth whereas those from the inner lines of the hyperfine spectra will be broader than the outer lines. Other assumptions are that K is uniaxial and does not depend upon temperature (known to be wrong) or volume. K may also depend upon the shape of the particles through different surface contributions. Interaction between the particles has been neglected. Also the Mössbauer lines have not been corrected for thickness broadening.

6. The blocking temperature T_B

T_B is not a transition temperature in the thermodynamic sense as it depends upon the time, τ_m, of the measurement. For susceptibility measurements, τ_m is usually taken to be 100 s. For Mössbauer spectra Wickman [8] quotes a smaller value of $\tau_m = 5 \times 10^{-9}$ s. So,

$$T_{B=} aKV/k \qquad (4)$$

where $a = 1/\ln(\tau_m/\tau_0)$.

Combined with the value of the anisotropy (Table 2) a value of about 0.2 is found for a. This gives $T_B = 133$ K (10.6 nm) and 37 K (5.3 nm). It is difficult to get precise values of T_B from the Mössbauer spectra because the spread in particles sizes broadens the transition region, but inspection of Figure 2 shows that these are of the right order of magnitude.

7. The characteristic time τ_0

The intercept with the time axis in Fig. 2 gives a value of about 10^{-11} s for Néel's characteristic time, τ_0. Previous estimates [7] on different materials range from 3.57×10^{-10} for α-Fe, and 1.05×10^{-11} for ferritin to 10^{-13} for Fe films.

8. Conclusions

The paper shows that the change in linewidth of the Mössbauer line in the region of the blocking temperature of magnetic nanoparticles can be used to deduce values for the magnetic anisotropy consistent with values deduced from low temperature measurements and consistent with the values of the blocking temperatures. This observation contributes to laying a foundation for the control over magnetic properties using nanoscience.

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