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Origin of Elevated Ordering Temperature in MnFe_2O_4 Nanometer Particles

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Abstract. Mössbauer spectra of MnFe_2O_4 with various particle sizes in a longitudinal 50 kOe magnetic field show that the Fe ion occupancy of the A and B crystallographic sites depends on the particle size. The elevated Néel temperatures with decreasing particle sizes are attributed to an increased iron occupancy on the A sites; this in turn leads to an increase in the total superexchange interaction.

1. INTRODUCTION

Tang et al [1] have reported that nanocrystalline powders of MnFe_2O_4 have enhanced ferrimagnetic Néel temperatures, T_{FN} , as compared to a bulk sample. They also show that the increases in T_{FN} can be described by a finite-size scaling formula. These findings have been supported by the EXAFS experiments of Kulkarni et al [2]. However van der Zaag et al [3], Brabers [4] and van der Zaag et al [5] suggest that the increase in ordering temperature is more likely to have its source in a redistribution of the iron and manganese cations over the tetrahedral (A) and octahedral (B) crystallographic sites of the spinel structure.

A powerful way to determine the cation distribution of a ferrimagnet is to employ applied-magnetic field ^{57}Fe Mössbauer spectroscopy at low temperatures (to ensure the recoilless fractions at the A and B sites are essentially the same). We have carried out this experiment and now report the results.

2. EXPERIMENTAL

The nanoparticles of MnFe_2O_4 with various particle sizes (15-30 nm) were prepared by coprecipitation, digestion and annealing at 500°C for 1 h in Ar, the identical procedures used by Tang et al [6] and by Kulkarni et al [2]. The annealing time is sufficient to ensure an equilibrium cation distribution.

X-ray diffraction patterns of three samples (a), (b) and (c) were taken using $\text{Cu } K_\alpha$ radiation. The difference in line broadenings for the three samples was evident even by visual inspection. Application of the Scherrer formula to

Table 1: Particle sizes and Néel temperatures for MnFe_2O_4 . The superscripts a and b represent the values obtained from x-ray diffraction and transmission electron microscope, respectively.

Sample	Size ^a (nm)	Size ^b (nm)	T_{FN} (K)
(a)	15	16	633
(b)	22	21	613
(c)	26	30	600

the (311) line was used to give the average crystallite sizes. The average particle sizes were also estimated from electron-microscope photographs. These results are listed in Table 1. The sizes obtained with the two techniques agree well for all three samples; this implies that the particles are single crystals, consistent with the conclusion of Tang et al [1]. The Néel temperatures were determined from a thermomagnetic scan in an applied field of 0.5 kOe; each scan was completed in 10-12 min in order to avoid the possibility of cation redistribution. The Néel temperatures, T_{FN} , also listed in Table 1, are elevated with decreasing particle sizes, in agreement with the earlier data [1,2].

^{57}Fe Mössbauer spectra of MnFe_2O_4 samples were collected at 300, 77 and 4.2 K with a conventional constant-acceleration spectrometer. In addition, Mössbauer spectra at 4.2 K were obtained with a 50 kOe longitudinal magnetic field applied. The source was ^{57}Co in a Rh matrix. Calibration was made using an $\alpha\text{-Fe}$ spectrum at room temperature. The Mössbauer spectra at 4.2 K were analyzed using one or two sextets with Lorentzian line shapes. For each sextet, the corresponding pairs of lines were constrained to have the same width and intensity.

3. RESULTS AND DISCUSSION

The Mössbauer spectra of MnFe_2O_4 at room temperature consist of a sextet plus a doublet for sample (a) and of a sextet for samples (b) and (c), as shown in figure 1 (A). The doublet has its origin in the superparamagnetism in the smallest particles. At 77 and 4.2 K, the Mössbauer spectra of all three samples consist of one sextet; the data at 4.2 K are shown in figure 1 (B). This sextet can be fitted using two overlapping sextet subpatterns, corresponding to iron nuclei on the A and B sites. However, the spectra can be fitted equally well with only one sextet. The implication is that the Mössbauer parameters for the A and B sites are about the same. It follows that for spectra obtained with no magnetic field applied, it is almost impossible to distinguish subspectra for the A and B sites, hence to infer accurately the distributions of the Fe and Mn ions over the two sites.

Figure 1: Mössbauer spectra of MnFe_2O_4 nanoparticles at (A) $T=300$ K, (B) $T=4.2$ K, both in zero applied field and (C) $T=4.2$ K in a longitudinal applied magnetic field of 50 kOe. The average particle diameter of the three samples is (a) 15 nm, (b) 22 nm and (c) 26 nm.

However, when an external magnetic field of 50 kOe is applied, the Mössbauer subspectra for the A and B sites are well separated, as shown in figure 1 (C). The reason is the applied field adds to the hyperfine field of the A-site nuclei and subtracts from that of the B-site nuclei. Therefore unambiguous Mössbauer parameters can be deduced for the two sites. The Mössbauer parameters, obtained by computer fitting, for MnFe_2O_4 in zero and 50 kOe fields are listed in Table 2.

It is important to note that the areas of the Mössbauer subspectra increase for the A site but decrease for the B site with decreasing particle size. This is strong evidence that the Fe occupancy of the A and B sites does depend on the particle size.

The values of the isomer shifts and quadrupole splittings indicate that all the iron ions are in the ferric (Fe^{3+}) state. Therefore, the structure formula of MnFe_2O_4 may be written as $(\text{Mn}_x^{2+}\text{Fe}_{1-x}^{3+})[\text{Mn}_{1-x}^{2+}\text{Fe}_x^{3+}]\text{O}_4$ where the round and square brackets refer to ions occupying A and B sites, respectively, and x is the distribution parameter. Since the

Table 2: Mössbauer parameters at 4.2 K in (A) zero field and (B) 50 kOe field for MnFe_2O_4 . δ is the isomer shift, relative to an α -Fe spectrum at room temperature; ϵ is the quadrupole splitting; H_{hf} is the hyperfine field; $A_{2,5}/A_{3,4}$ is the area ratio between the 2nd plus 5th lines and the 3rd plus 4th lines; S is the relative subspectral area; $\langle\theta\rangle$ is the average canting angle.

(A) zero field							
Sample		δ (mm/s)	ϵ (mm/s)	H_{hf} (kOe)			
(a)		0.14(2)	-0.03(2)	505(5)			
(b)		0.13(2)	-0.03(2)	511(5)			
(c)		0.15(2)	-0.03(2)	511(5)			

(B) 50 kOe field							
Sample	Site	δ (mm/s)	ϵ (mm/s)	H_{hf} (kOe)	$A_{2,5}/A_{3,4}$	S (%)	$\langle\theta\rangle$
(a)	A	0.06(2)	-0.06(2)	552(5)	0.68(5)	23.8(7)	33(1)
	B	0.13(2)	-0.01(2)	464(5)	0.68(5)	76.2(11)	33(1)
(b)	A	0.03(2)	-0.04(2)	565(5)	0.55(4)	20.4(8)	30(1)
	B	0.15(2)	-0.02(2)	469(5)	0.55(4)	79.6(11)	30(1)
(c)	A	0.04(2)	-0.05(2)	564(5)	0.40(4)	18.1(8)	25(1)
	B	0.15(2)	-0.01(2)	465(5)	0.40(4)	81.9(13)	25(1)

absorbers were relatively thin and at 4.2 K the recoilless fractions for iron ions on the A and B sites are essentially equal, the occupation numbers of the iron ions are proportional to the corresponding areas of their Mössbauer spectra. Consequently, the value of x can be obtained from the relative areas of the Mössbauer subspectra for the A and B sites. The results are listed in Table 3 together with data for a bulk sample [7].

Based on a mean field theory by Lotgering [8], the Néel temperature, T_{FN} , of MnFe_2O_4 can be expressed as

$$T_{FN}^4 - \{x(1-x)N_{MnMn}^2(AB) + (1-x)(1+x)N_{FeFe}^2(AB) + [x(1+x) + (1-x)^2]N_{FeMn}^2(AB)\}T_{FN}^2 + x(1+x)(1-x)^2\{N_{FeFe}(AB)N_{MnMn}(AB) - N_{FeMn}(AA)N_{FeMn}(BB)\}^2 = 0 \quad (1)$$

where $N_{ab}(AB)$ represents the molecular field coefficient of ions a and b associated with the superexchange interaction between the A and B sublattices, respectively, and a similar notation for the intrasublattice interactions (AA) and (BB). In the analysis by Lotgering [8] for MnFe_2O_4 , the intrasublattice interactions are relatively weak and can be neglected, the $\text{Mn}(A)\text{Mn}(B)$ interaction can also be neglected since it is much weaker than the $\text{Fe}(A)\text{Fe}(B)$ and $\text{Fe}(A)\text{Mn}(B)$ ones, and finally $N_{FeFe}(AB) \simeq 2N_{FeMn}(AB)$. The values of T_{FN} and x from Tables 1 and 3 substituted into eq.(1) yield $N_{FeMn}(AB) = 318$ K. The Néel temperatures calculated as a function of x are shown as the solid curve of figure 2. The consistency between the calculated and the experimental values provide strong evidence that the elevated Néel temperatures can be attributed to the increased Fe occupancy on the A sites which in turn leads to an increase in the total superexchange interaction.

In figure 1 (C), the non-zero 2nd and 5th lines indicate that a non-collinearity is present in the magnetic structure. The average canting angles, $\langle\theta\rangle$, are obtained from the ratio of the 2nd plus 5th to the 3rd plus 4th line areas by the equation

$$\langle\theta\rangle = \cos^{-1} \sqrt{\frac{4 - A_{2,5}/A_{3,4}}{4 + A_{2,5}/A_{3,4}}} \quad (2)$$

The values of $\langle\theta\rangle$ from the data are listed in Table 2 and plotted in figure 3. Obviously, the canting angles increase with decreasing particle size. This may indicate that the non-collinearity lies in a surface effect.

Table 3: Cation distributions for MnFe_2O_4 with average particle sizes (a) 15 nm, (b) 22 nm and (c) 26 nm. (d) is for a bulk sample [7].

Sample	Structure formula	Sample	Structure formula
(a)	$(\text{Mn}_{0.52}\text{Fe}_{0.48})[\text{Mn}_{0.48}\text{Fe}_{1.52}]\text{O}_4$	(b)	$(\text{Mn}_{0.59}\text{Fe}_{0.41})[\text{Mn}_{0.41}\text{Fe}_{1.59}]\text{O}_4$
(c)	$(\text{Mn}_{0.64}\text{Fe}_{0.36})[\text{Mn}_{0.36}\text{Fe}_{1.64}]\text{O}_4$	(d)	$(\text{Mn}_{0.80}\text{Fe}_{0.20})[\text{Mn}_{0.20}\text{Fe}_{1.80}]\text{O}_4$

Figure 2: Calculated Néel temperatures (T_{FN}) as a function of cation site occupancy based on mean-field theory. The data point (■) is for a bulk sample (ref. [7]).

Figure 3: The average canting angle, $\langle \theta \rangle$, as a function of particle size for MnFe_2O_4 .

4. CONCLUSIONS

Mössbauer spectra of MnFe_2O_4 in a longitudinal 50 kOe magnetic field exhibit clearly resolved subspectra associated with iron ions the A and B sites (in contrast to zero-field spectra). The cation distribution on the A and B sites depends on the particle size. Based on the mean-field theory, the Néel temperatures calculated as a function of the cation distribution parameter agree well with the experimental data. It is concluded that the origin of the increased ordering temperatures is the result of an increased iron occupancy on the A sites and not on finite-size scaling.

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