Size-dependent magnetic properties of MnFe₂O₄ fine particles synthesized by coprecipitation

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Manganese ferrite, $MnFe_2O_4$, fine particles in the size range 5–15 nm have been prepared by an aqueous phase coprecipitation method. The freshly prepared particles are in a metastable state with regard to the cation distribution between the *A* and *B* sites of the spinel lattice. Thermomagnetic, differential scanning calorimetry and Mössbauer spectroscopy show that heat treatment under inert gas to 670 K irreversibly changes the cation distribution to a stable state. Heat treatment of freshly prepared samples in air to 470 K both changes the cation site distribution somewhat and, most importantly, oxidizes the Mn^{2+} to Mn^{3+} . The Curie temperature is modified in association with these changes. With this knowledge, we create a series of samples with various sizes but the same microstructure. We find the following. (1) The Curie temperature decreases relative to the bulk as size decreases. The decrease is consistent with finite size scaling. (2) The fit of the spontaneous magnetization to the Bloch $T^{3/2}$ law yields a Bloch constant larger than the bulk increasing with decreasing size in proportion to the specific surface area of the particles. We find a better fit is obtained if the exponent of the temperature is increased to be in the range 1.6 to 1.8. (3) The saturation magnetization decreases with decreasing size also in proportion to the specific surface area of the particles. [S0163-1829(96)02238-2]

I. INTRODUCTION

The magnetic properties of nanoscale particles have been a subject of interest in the past decade.^{1,2} Two major reasons may be cited for this interest: increasing miniaturization and data storage densities require knowledge of the properties of nanoscale systems and basic curiosity of how bulk properties transform to the atomic as the size is decreased.

In this work we have studied size effects on the magnetic properties of manganese ferrite, MnFe₂O₄, particles, in particular the Curie transition and the magnetization. MnFe₂O₄ is well suited for such a study because it has a relatively low Curie temperature, 300 °C, which allows for the study of the transition from ferrimagnetic order to paramagnetic states before thermal effects cause the particles to become superparamagnetic. A disadvantage of MnFe₂O₄ is that it is a complex system. Previous work³⁻⁶ has shown that manganese ferrite prepared by aqueous phase precipitation can have different characteristics than those prepared by classical ceramic methods (involving high temperature reaction), especially in their magnetic saturation and coercive field strengths, as well as their obvious color change. In Mössbauer^{7,8} and neutron scattering studies,^{5,9–11} it has been found that the inversion degree of the distribution of the cationic ions between the tetrahedral and octahedral sites of the spinel lattice in precipitated MnFe₂O₄ was higher than in those prepared by ceramic methods. This inversion degree can also be changed by an appropriate heat treatment of the

samples at rather low temperature.¹² In previous work¹³ some of us reported an increase in the Curie temperature of $MnFe_2O_4$ particles with decreasing size. At that time we reported that this change in T_C was consistent with finite size scaling. The work we present here now leads us to believe that this increase was a result of different degrees of inversion of the spinel lattice due to Mn^{2+} to Mn^{3+} oxidation as a function of size.

Because of the importance of these site inversion phenomena, the first part of the paper is focused on the effects of heat treatment on the magnetic properties of $MnFe_2O_4$ particles to clarify the structural change during heating and to explain our previous experimental results.¹³ Once these site inversion phenomena are understood and controlled, we are able to use our particles for our original motive: size dependent studies. We now find a decreasing Curie temperature and an increasing Bloch constant and deviations from the Bloch law all with decreasing size. These changes can be empirically related to either surface effects or possibly finite size scaling.

II. SYNTHETIC METHODS

The MnFe₂O₄ particles were synthesized by coprecipitation followed by digestion.¹⁴ The starting materials were FeCl₃· $6H_2O$ and MnCl₂· $4H_2O$. Sodium hydroxide, NaOH, was used as the reaction agent. The reaction is described by

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$$MnCl_2 + 2FeCl_3 + xNaOH \rightarrow MnFe_2O_4$$
$$+ (x - 8)NaOH + 4H_2O + 8NaCl, \qquad (1)$$

where the variable $x \ge 8$ represents the relative amount of NaOH. MnCl₂ \cdot 4H₂O and FeCl₃ \cdot 6H₂O were dissolved in water at concentrations of 0.05M and 0.1M, respectively, under the condition of $[Fe^{3+}]/[Mn^{2+}]=2:1$. Then the solution was slowly poured into a well stirred 3M NaOH solution, which lead to a precipitation of particles. After the reaction, the suspension was put into a sealed, temperature controlled reaction vessel for digestion. It has been found that the pHvalue and digestion temperature and time affect the particle size and morphology.^{14,15} The digestion was performed at 100 °C for 90 min. During digestion, the particles grew and evolved from an amorphous structure to a single crystal structure. By varying x so that the ratio ($[Mn^{2+}]$) $+[Fe^{3+}]$:[OH] varied from 0.02 to 0.375, the average particle size at equilibrium could be varied from 5 to 25 nm. After digestion, the suspension was repeatedly washed and filtered before drying at room temperature in air to form a powder sample.

III. CHARACTERIZATION OF THE PARTICLES

The morphology of MnFe₂O₄ particles was studied by transmission electron microscopy (TEM) and x-ray diffraction (XRD). Figure 1 shows the TEM pictures of both a nondigested sample and a digested one. The nondigested MnFe₂O₄ particles were tiny and amorphous with an average particle size of 4 nm, independent of reaction conditions. After digestion, the particles had a cubic crystal structure. A few tiny particles can be observed surrounding the larger crystals. Shown in Fig. 2 are the XRD spectra for the asprepared and digested samples. The spectrum for the undigested particles has two broad peaks without any structure. After digestion, several peaks appear, all corresponding to MnFe₂O₄. The crystallite size of the digested sample was calculated with the Scherrer formula¹⁶ and the particle size was determined by means of gas adsorption with the Brunauer, Emmett, and Teller (BET) method.¹⁷ The crystallite size was found to be 10% to 20% larger than the particle size determined from BET measurement. This may result from the tiny particles surrounding the large crystals. X ray is more sensitive to large crystallites, while the BET method measures the average particle size. This reasonable correlation between the sizes determined by the two methods implies the particles after digestion were single crystals.

IV. EFFECTS OF HEAT TREATMENT ON MnFe₂O₄

A. Heated in inert gas

The temperature dependence of the magnetization of $MnFe_2O_4$ particles was studied with a superconducting quantum interference device (SQUID) magnetometer. A freshly prepared sample was heated in the SQUID from room temperature to 670 K and then cooled to room temperature, while magnetic data were collected in a magnetic field of 50 Oe. Figure 3 shows the behavior of a $MnFe_2O_4$ sample with an average diameter of 11.5 nm (from BET measurement). With increasing temperature, the magnetization was approximately constant until a large drop occurred beginning at 570



FIG. 1. TEM pictures of coprecipitated $MnFe_2O_4$ particles before digestion (a), and after digestion (b).

K. This indicates a ferrimagnetic to paramagnetic transition. The Curie temperature (T_C) , which was determined by the intersection of the tangent line at the largest slope with the flat bottom, was 610 K. When the sample was subsequently cooled to room temperature and reheated in an identical manner, it showed a different transition at 570 K, the same as the T_C of bulk MnFe₂O₄ synthesized by ceramic methods.¹⁸ After the initial measurement, the transition temperature became fixed at 570 K regardless of increasing or decreasing temperature.

Differential scanning calorimetry (DSC) was used to investigate this phenomenon further. Shown in Fig. 4 is the heat flowing into a fresh sample [curve (a)] as temperature increased linearly (20 °C/min). Curve (b) shows the behavior of the same sample for a second run. For the fresh sample a large dip was found at 400 °C (673 K) implying an exothermic transition. On the other hand, for the second run, the curve is smooth at 400 °C, suggesting an irreversible transition happened during the first run. The wide trough around 250 °C might imply some change which we have not yet determined.

The magnetic and thermal data yield a consistent picture for the precipitated $MnFe_2O_4$ particles: the structure of the as-prepared precipitated particles is unstable and can be al-



FIG. 2. X-ray diffractogram for an as-prepared sample (a) and a digested sample (b).

tered by heat treatment. The as-prepared particles have a higher Curie temperature than the annealed particles. The structural transition happens at 673 K and is irreversible.

What caused this transition? The x-ray spectrum did not show any change in crystal structure after heating. Previous work¹² showed that heating may change the distribution of metal ions in the tetrahedral and octahedral sites of MnFe₂O₄. The distribution of metal ions between tetrahedral and octahedral sites of MnFe₂O₄ prepared by ceramic methods has been determined by neutron diffraction experiment^{9,10} to be 81% normal, i.e., $Mn_{0.81}Fe_{0.19}[Mn_{0.19}Fe_{1.81}]O_4$ where cations in brackets occupy octahedral sites. Here and subsequently "normal"



FIG. 3. Temperature dependence of magnetization of fresh $MnFe_2O_4$ particles with an average diameter of 11.5 nm. Arrows indicate direction of temperature change.



FIG. 4. DSC spectrum of $MnFe_2O_4$ particles measured when the temperature increased. d=11.5 nm. (a) As prepared, and (b) post heat treated.

means that all the manganese is on the tetrahedral sites, hence none on the octahedral sites, of the spinel lattice, and conversely "inverted" means that the manganese is on the octahedral sites. Other experiments have given a slightly different, but similar distribution.⁷ On the other hand, $MnFe_2O_4$ produced from aqueous solution have been found to have a quite different distribution by NMR (Ref. 4) and neutron diffraction.⁵ The neutron diffraction experiment has shown that $MnFe_2O_4$ prepared from wet chemical methods is 33% normal, which means a distribution of $Mn_{0.33}Fe_{0.67}[Mn_{0.67}Fe_{1.33}]O_4$. The phase transition observed in our samples may be the result of a site redistribution, hence a high field Mössbauer study was performed to determine the exact distribution of Fe^{3+} and Mn^{2+} in the A and B sites.

The Mössbauer spectrum was taken with a magnetic field applied perpendicular to the direction of propagation of the 14.4 keV γ rays of ⁵⁷Fe. Spectra of an as-prepared sample were collected at 4.2 K in zero field and in an applied field of 60 kOe. The zero-field spectrum consists of six absorption lines (one sextet), whereas the high field spectrum consists of two sextets (Fig. 5). The existence of two sextets in an applied field is due to the two sublattices (*A* and *B* sites) whose spins are antiparallel. Without an applied field, the difference between hyperfine fields at site *A* and *B* is not large enough to separate the two sextets. With an applied field, B_0 , the difference of the hyperfine field at the *A* and *B* sites is increased by $2B_0$.

Distributions of Fe³⁺ ions in the *A* and *B* sites can be determined by comparing the relative area covered by the sextets from the *A* and *B* sites. This was done by fitting Mössbauer spectra into Lorentzian-shaped profiles (least squares fit). The Mössbauer spectra for the as-prepared and annealed samples in an applied field of 60 kOe are shown in Fig. 5. The related data derived from them are listed in Table I with the error in the cation distribution of ± 0.05 . We note that the intensity of the $\Delta m = 0$ lines ($I_{2,5}$) normalized to an intensity of 3 for the $\Delta m = \pm 1$ lines is lower than 4, implying an angle of the magnetic moments from the magnetic field different than zero. In the case of the samples annealed in inert atmosphere this ratio is different for the *A* and *B* sites, and the magnitude of the difference would imply a



FIG. 5. Mössbauer spectra of MnFe₂O₄ particles at 4.2 K with a field of 60 kOe perpendicular to the direction of propagation of the Fe⁵⁷ γ rays for d=11.5 nm. (1) As prepared, (2) annealed in SQUID, and (3) annealed in Ar at 200 °C for 6 h.

deviation from collinearity between the two sites of about 10°. The ratio of areas of the *A* and *B* sites gives the ratio of the number of Fe atoms in the *A* and *B* sites, respectively. If we assume that the overall stoichiometry of the sample is $MnFe_2O_4$, we calculate the cation distributions as $Mn_{0.33}Fe_{0.67}[Mn_{0.67}Fe_{1.33}]O_4$ for the as-prepared sample, similar to previous work,⁵ and $Mn_{0.60}Fe_{0.40}[Mn_{0.40}Fe_{1.60}]O_4$ for the annealed samples, lower than those synthesized with ceramic methods. We conclude that heat treatment in inert gas irreversibly alters the cation distribution.

The results of these Mössbauer spectra can be used to qualitatively explain the change of the Curie temperature with heat treatment. Since the exchange interaction between

TABLE II. Magnetic and structural properties of the MnFe₂O₄ samples with d=11.5 nm annealed in air at 200 °C. The peak shift is the shift of the peak at $2\theta=61.6^{\circ}$ in the XRD spectrum. The coercivity (H_C) and saturation magnetization (σ_s) were measured at 10 K.

Sample	Heating time (h)	Peak shift (deg)	Т _С (К)	H _C (Oe)	σ_s (emu/g)
1	0	0.17	610	196	81.1
2	1	0.57	651	289	67.5
3	2	0.63	658	427	65.2
4	4	0.67	662	431	64.0
5	6	0.77	664	498	68.1
6	12	1.0	722	569	57.8

 Fe^{3+} ions in *A* and *B* sites is bigger than that between Mn^{2+} in *A* site and Fe^{3+} in *B* site, ^{12,19,20} the increase of the degree of inversion causes the average exchange interaction to increase. This in turn causes the Curie temperature to increase.¹² This explains why the as-prepared sample which has a larger inversion degree has a higher Curie temperature, while the annealed sample which has a lower inversion degree has a lower Curie temperature.

B. Heated in air

Compared to the effects of heat treatment in inert gases described above, annealing in air has dramatically different effects on MnFe₂O₄ particles. Samples with average diameter of 11.5 nm were heated at 200 °C in air for 1, 2, 4, 6, and 12 h. Although their crystal structure was still spinel as shown in the x-ray diffraction spectra, the characteristic peaks shift to larger angles with increasing heating time. Table II lists these peak shifts as well as the measured magnetic properties of this set of samples. As heating time increases, Curie temperature and coercivity increase. However, the saturation magnetization decreases with the increase of heating time. These observations are very different from what we discussed in the last section, where a decreasing Curie temperature for samples heated in inert gas was observed. Furthermore, once heat treated in air at 200 °C, there was no structural change at 400 °C as described above.

The Mössbauer spectra for samples annealed in air are shown in Fig. 6 and results of fits to these spectra are given in Table III. The stoichiometries are calculated under the same assumption as with the samples annealed in inert atmo-

TABLE I. Isomer shift and hyperfine field at the A and B sites derived from Fig. 5 (1) as-prepared, (2) annealed in SQUID, and (3) annealed in Ar at 200 °C for 6 h.

	IS(m	IS(mm/s) ^a		HF(T) ^b		,5 [°]	
Sample	Α	В	Α	В	Α	В	Distribution
1	0.40	0.50	51.3	52.2	3.3	3.2	Mn _{0.33} Fe _{0.67} [Mn _{0.67} Fe _{1.33}]O ₄
2	0.38	0.51	50.8	51.7	2.8	3.4	Mn _{0.63} Fe _{0.37} [Mn _{0.39} Fe _{1.63}]O ₄
3	0.37	0.51	50.6	51.7	2.9	3.3	$Mn_{0.60}Fe_{0.40}[Mn_{0.40}Fe_{1.60}]O_4$

^aIsomer shift (IS) relative to α -Fe.

^bHyperfine field (HF).

^cThe intensity of peaks 2 and 5 ($I_{2,5}$) normalized on the condition of $I_{1,6}=3$. $I_{2,5}$ should be 4 if collinear.



FIG. 6. Mössbauer spectra of MnFe₂O₄ particles at 4.2 K with a field of 60 kOe perpendicular to the direction of propagation of the ⁵⁷Fe γ rays for d=11.5 nm. (1) As prepared, (2) annealed in air at 200 °C for 6 h, and (3) annealed in air at 200 °C for 12 h.

sphere. The spectra indicated that the inversion degree was not strongly related to the heating time. Samples heated for 6 and 12 h are both 43% normal and have the same isomer shift and hyperfine field even though the other properties of these two samples are different (Table III). These results imply that the heating effects on the magnetic properties are not the result of the redistribution of metal ions in the A and B sites. Recall that inversion degree of the same size sample heated in inert gases reaches about 60% normal and yet has a smaller Curie temperature. This leaves the possibility that the oxygen in the air may play an important role in the property changes.

The oxidation explanation relies on the assumption that Mn^{2+} is oxidized to Mn^{3+} by the oxygen in the air. Mn^{3+} has a relatively higher crystal field stabilization energy for octahedral coordination. Thus it tends to stay at the octahedral B site.²¹ This oxidation process may cause some defects in the $MnFe_2O_4$ structure because there must be some charge compensation, and it is unlikely that Fe would become divalent. It is possible that cation vacancies are created. This explanation is supported by the work done by Tailhades and co-workers.²² Mn³⁺, a d^4 ion, is subject to Jahn-Teller distortion in octahedral coordination. This can cause the x-ray characteristic peak positions to shift, as observed, but not change the spinel structure. Jahn-Teller distortion will cause large local strain, which leads to an increase of the crystal anisotropy²³ hence a larger coercivity, also as observed. The increase of the Curie temperature may be the result of the contraction of the lattice. Pressure experiments with Fe₃O₄ indicate an increase of Curie temperature with pressure.²⁴ The magnetic moments of Mn^{2+} and Mn^{3+} ions and $5\mu_B$ and $4\mu_B$, respectively. With the oxidation of Mn²⁺ to Mn³⁺, the net magnetic moment of lattice B decreases. Therefore, the net magnetic moment of MnFe₂O₄ decreases correspondingly, again as observed. With increasing heating time, more Mn²⁺ ions are oxidized to Mn³⁺. Since all the Mössbauer spectra showed a noncollinear arrangement of spins $(I_{2.5})$ should be 4 if collinear), it is difficult to get any quantitative information on the exact fraction of Mn^{3+} that is oxidized. Despite this, our qualitative explanation works very well. A similar description of air oxidation effects has recently also been proposed by van der Zaag et al.²⁵

In light of these conclusions we also remark that in the absence of oxygen well annealed stoichiometric $MnFe_2O_4$ can have a very low degree of inversion on the order of a few percent.²⁶ Thus the large 67% degree of inversion in our as-prepared particles implies that they may already have a cation deficient lattice with Mn^{3+} on the octahedral sites.²⁶

Our previous experimental results on $MnFe_2O_4$ particles synthesized by coprecipitation¹³ showed no phase transition as discussed in the previous section (IV A), and the T_C increased by as much as 97 K with decreasing particles size. This has caused some discussion.^{27–29} Now we think this was the result of heat treatment in air. Previously, the wet particles were dried on a hot plate in air, at a temperature of about 100 °C, and subsequently annealed at 500 °C for an hour.³⁰ As shown above, heat treatment in air causes a structural change in MnFe₂O₄ particles most likely due to oxidation of Mn²⁺ to Mn³⁺. This results in a higher Curie tem-

TABLE III. Isomer shift and hyperfine field in *A* and *B* sites derived from the Mössbauer spectra in Fig. 6. (1) As-prepared, (2) annealed in air at 200 °C for 6 h, and (3) annealed in air at 200 °C for 12 h.

	IS(m	IS(mm/s) ^a		HF(T) ^b		,5 [°]	
Sample	Α	В	Α	В	Α	В	Distribution
1	0.40	0.50	51.3	52.2	3.3	3.2	Mn _{0.33} Fe _{0.67} [Mn _{0.67} Fe _{1.33}]O ₄
2	0.37	0.50	51.1	51.9	3.3	3.3	Mn _{0.43} Fe _{0.57} [Mn _{0.60} Fe _{1.40}]O ₄
3	0.37	0.44	50.8	51.9	3.3	3.3	$Mn_{0.43}Fe_{0.57}[Mn_{0.60}Fe_{1.40}]O_4$

^aIsomer shift (IS) relative to α -Fe.

^bHyperfine field (HF).

^cThe intensity of peaks 2 and 5 ($I_{2,5}$) normalized on the condition of $I_{1,6}=3$. $I_{2,5}$ should be 4 if collinear.



FIG. 7. Size dependence of Curie temperature for the Asprepared samples and the annealed samples.

perature. It is reasonable to propose that the smaller particles oxidize more rapidly than the larger particles and hence will have larger T_C , as we observed. We believe this is a suitable explanation of our previous results. Again we note that van der Zaag *et al.*²⁵ have recently proposed the same explanation.

In general, $MnFe_2O_4$ is a complicated system. Its properties can be affected by synthetic method, heating temperature, heating time, introduction of oxygen, and cooling rate. In the study of this system, every condition must be well under control to obtain reproducible results.

V. FINITE SIZE EFFECT ON THE CURIE TEMPERATURE

As we have learned, if we are to study size effects on the magnetic properties of fine particles, it is important that the samples of different sizes have the same microstructure. The results above show us how to create particles with the same microstructure and allow us flexibility in that the size effects on two different microstructures can be studied and compared. The samples used in this study were as-prepared and those annealed under helium in the SQUID as a result of the initial T_C measurement on the as-prepared particles. As described above, the as-prepared particles were synthesized by precipitation followed by digestion and dried at room temperature. No heat treatment was done on any of these samples to avoid structural change. The Curie temperature (T_c) of a fresh, as-prepared sample was measured in a 50 Oe field as temperature increased. After the temperature reached 670 K, the sample was cooled and the Curie temperature of the annealed sample was measured. The particle size was measured before and after the Curie temperature measurement by BET. No size change was found within the experimental error.

The relation between Curie temperature and particle size is shown in Fig. 7. The behaviors of the as-prepared and annealed particles are quite similar, except a temperature shift which is due to the change in the A and B site distribution as explained in Sec. IV A. T_C shows a decrease with decreasing particle size especially below 10 nm.

We propose that this decline in Curie temperature could



FIG. 8. Reduced Curie temperature $[(T_{\infty}-T_d)/T_{\infty}]$ of the MnFe₂O₄ particles as a function of particle size.

be due to either of two causes, finite size scaling or a surface effect. The finite size scaling theory predicts that the shift in the transition temperature from that of the bulk should depend on the size of the system in the following manner:³¹

$$\frac{T_C(\infty) - T_C(d)}{T_C(\infty)} = (d/d_0)^{-1/\nu},$$
(2)

where $T_C(d)$ is the Curie temperature as a function of particle size d, $T_C(\infty)$ is the bulk Curie temperature, d_0 is a constant, and ν is the critical exponent of the correlation length. The change in T_C may be positive or negative depending on boundary conditions, geometry, and interaction. Finite size scaling has been observed in two-dimensional systems, such as transition metal thin-film systems³² and rare-earth/nonmagnetic multilayers.³³

It is also possible that T_C decreases due to some unknown surface effect. For small particles a significant fraction of atoms is on the surface, and it is reasonable to expect their magnetic interaction to be different hence a different average Curie temperature. Since the ratio of surface to bulk atoms in a particle is proportional to d^{-1} , such an effect, if linearly dependent on the specific surface area, might yield a change in T_C proportional to d^{-1} which would be mathematically equivalent to Eq. (2) with $\nu=1$ (and an entirely different physics). Such behavior for other properties has been seen before (see³⁰ and below).

By fitting both sets of data in Fig. 7 to Eq. 2, $T_C(\infty)$, d_0 , and ν were obtained. Figure 8 shows the results of the fitting. The best fits are

$$T_C(\infty) = 625 \pm 5$$
 K (as prepared),

$$T_C(\infty) = 585 \pm 5$$
 K (annealed)

and for each

$$\nu = 0.5 \pm 0.2, \quad d_0 = 17 \pm 7$$
 Å.

The quoted errors are one standard deviation. The value of $T_C(\infty)$ for the annealed samples is higher than the known bulk value of MnFe₂O₄ prepared by ceramic methods (573 K),¹⁸ but reasonable given the fact that the degree of inver-



FIG. 9. (a) Spontaneous magnetization as a function of temperature measured in a field of 55 kOe for the particles with an average diameter of 8.8 nm and the result of the fitting to Eq. (3). (b) The difference between the experimental data and the fitting results.

sion of our annealed samples is higher than that of $MnFe_2O_4$ synthesized by ceramic methods and T_C increases with this inversion.

The fit value of $\nu=0.5\pm0.2$ is consistent, within the large error, with the known value of ν for magnetic systems which is in the range 0.65 ± 0.07 .^{34,35} Also the fit value of d_0 , which is comparable to the lattice constant, is reasonable. Thus our data are consistent with finite size scaling. On the other hand, a possible surface effect in which the temperature shift is proportional to d^{-1} does a less satisfactory job of describing the data, although such an effect cannot be ruled out on the basis of our qualitative argument. Furthermore, an unknown surface effect different than that which we have envisioned cannot be ruled out. Given the scatter in the data evident in Fig. 7, a realistic appraisal is that although the data may be satisfactorily described by finite size scaling, they lack the precision necessary to quantitatively demonstrate that finite size scaling explains the shift.

VI. SIZE EFFECTS ON THE BLOCH LAW

The spontaneous magnetization was measured in a field of 55 kOe to force all the MnFe₂O₄ particles to align in the same direction. For an infinitely large ferrite system, the spontaneous magnetization σ at low temperature should follow the Bloch law^{36–38}

$$\sigma = \sigma(0)(1 - BT^{3/2}), \qquad (3)$$

where $\sigma(0)$ is the spontaneous magnetization at zero kelvin and *B* is the Bloch constant. Figure 9 shows the typical be-



FIG. 10. Bloch constant of $MnFe_2O_4$ particles as a function of the inverse of the particle size.

havior of MnFe₂O₄ particles at low temperature and the results of fitting the data to Eq. (3). The Bloch constants obtained in this manner increased as the particle size decreased. These values are shown in Fig. 10 as a function of the inverse of particle size. The roughly linear relationship with d^{-1} suggests that the increase of *B* is related to the increase of the specific surface area of the particles.

The deviation plot in Fig. 9 shows systematics that could not be eliminated unless the 3/2 exponent in Eq. (3) was allowed to vary. Fitting to $\sigma(T) = \sigma(0)(1 - B'T^{\alpha})$ led to α values in the range of 1.6 to 2.0 as shown in Fig. 11. We expect $\alpha = 1.5$ for bulk samples; thus the trend in our results, that α in Fig. 11 seems to be approaching 1.5 from larger values as size decreases, is unexpected. The implication is that if a wide range of sizes were available α would display a maximum at some intermediate size.

Theoretical calculations on ferromagnetic materials^{39,40} have shown that the fluctuation of the surface moments is larger than the interior. Mills *et al.*³⁹ found the magnetization of fine particles obeys the Bloch law and the Bloch constant



FIG. 11. The exponent of the modified Bloch law, α , as a function of particle size.



FIG. 12. Saturation magnetization as a function of particle size.

is 2–3 times larger than the bulk. However, the calculation of Hendriksen and co-workers⁴⁰ for ferromagnetic materials shows that finite size causes a large deviation from the normal Bloch $T^{3/2}$ law for the spontaneous magnetization at low temperature; they found instead close to an effective T^2 dependence. Although our system is a ferrimagnetic material, it has similar behaviors as predicted for ferromagnetic materials.

The characteristics of the Bloch constant for these samples suggest that with the increase of temperature the spontaneous magnetization decreases faster for small particles than for the bulk. It also implies that the spins in small particles are more unstable than those in the bulk materials,⁴⁰ which in turn leads to the drop of the Curie temperature relative to the bulk materials. Such behavior has been previously reported for 4 nm α -iron particles⁴¹ and nickel particles.⁴²

VII. SIZE EFFECT ON THE SATURATION MAGNETIZATION

The saturation magnetization of $MnFe_2O_4$ particles was found to be smaller than the bulk value and decreased with decreasing particle size. Figure 12 shows the saturation magnetization of $MnFe_2O_4$ particles at 10 and 300 K plotted against 1/d. It can be well fitted by a straight line. This phenomena has been observed in several ferrite system^{43,44} and was explained by a magnetically dead layer on the surface of particles.⁴⁵ Assuming the thickness (t) of the dead layer is a constant, the magnetization of the particles to first order is

$$\sigma_s = \sigma_s(\text{bulk}) \left(1 - \frac{6t}{d} \right). \tag{4}$$

Fitting the data in Fig. 12 with Eq. (4), we obtain $\sigma_s(\text{bulk})=110$ and 80 emu/g at 10 and 300 K, respectively, which are the same as those measured in bulk materials.¹⁸ The thickness of the dead layer obtained from the fitting is 5 Å at 10 K and 6 Å at 300 K. Therefore, our data support the dead layer theory. The existence of the nonmagnetic layer might be caused by the canting of the surface spins,^{46–48} a high anisotropy layer, or loss of the long range order in the surface layer⁴⁹ or other reasons. Our Mössbauer data strongly suggest the existence of spin canting in MnFe₂O₄ particles, but we cannot confirm if the spin canting only happens on the surface layer.

VIII. CONCLUSIONS

The aqueous phase coprecipitation method of synthesis of $MnFe_2O_4$ particles yields particles in a metastable site distribution $Mn_{0.33}Fe_{0.67}[Mn_{0.67}Fe_{0.33}]O_4$. This phase can be irreversibly altered to Mn_{0.60}Fe_{0.40}[Mn_{0.40}Fe_{1.60}]O₄ by heating under inert gas at 670 K or to $Mn_{0.43}Fe_{0.57}[Mn_{0.60}Fe_{1.40}]O_4$ by heating in air at 470 K. Heat treatment in air also oxidizes some Mn^{2+} to Mn^{3+} and causes a Jahn-Teller distortion. Control of the wet synthesis allows control of particles size and in light of results above control of the subsequently heat treatment allows control of the particle microstructure. Consequently we studied size dependent effects on the Curie temperature and magnetization of two sets of particles with different microstructure. We find T_C decreases with particle size in a manner consistent with finite size scaling. On the other hand, increases in the Bloch constant and decreases in the saturation magnetization with decreasing size were well described by a surface effect. Finally deviations from the Bloch $T^{3/2}$ law were observed for our nanometer particles.

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