

# Size-dependent magnetic properties of manganese ferrite fine particles

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We have developed synthetic techniques involving coprecipitation of iron(III) and manganese(II) ions from aqueous solutions using NaOH to create single-crystal, stoichiometric  $\text{MnFe}_2\text{O}_4$  particles. The particle diameter could be varied between 5 and 25 nm by varying the metallic-ion to hydroxide-ion concentration ratio. Magnetic measurements revealed that the saturation magnetization decreased, the ferrimagnetic to paramagnetic transition broadened, and the apparent transition temperature increased, all with decreasing particle size.

## I. INTRODUCTION

Particle size has significant effect on the magnetic properties of fine particles. Past work has shown changes of magnetization and coercivity caused by the changing size.<sup>1-5</sup> Attention has also been paid to the phase-transitional properties of ultrathin films to search for finite-size effects.<sup>6-8</sup> In this paper, we describe the preparation of the fine  $\text{MnFe}_2\text{O}_4$  particles by coprecipitation and our initial effort to investigate size effects on the magnetic properties and transition temperature of these fine particles.

## II. EXPERIMENTAL METHODS

The fine manganese ferrite ( $\text{MnFe}_2\text{O}_4$ ) particles were prepared by a coprecipitation method and subsequent digestion (aging) process. A detailed study of this synthesis has been performed.<sup>9</sup> The following procedures were used to create the particles studied in this work: (1) Dissolve  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  salts in distilled and de-ionized water. The total molarity of the metallic ions calculated for the final solution volume (after addition of the NaOH solution, below) ranged from 0.015 to 0.25 mol. The atomic ratio of Mn to Fe was 0.5. (2) Dissolve NaOH in water. The molarity was from 0.5 to 2.5 mol. (3) Pour the metallic solution slowly into the hydroxide solution while continuously stirring with a magnetic stirrer to yield a dark precipitate. (4) The beaker which contained the precipitate was brought into a preheated bath of water and ethylene glycol for digestion. Digestion was performed at 100 °C for 90 min, which was long enough to reach the equilibrium particle size.

X-ray diffraction, chemical analysis, Brunauer, Emmett, and Teller (BET) adsorption measurement, and vibrating sample magnetometer (VSM) were then used to characterize the particles. The ferrite phase was examined by x-ray diffraction, and the atomic ratio of the metallic elements was determined by chemical analysis. Two techniques were used to measure the particle size. One was by the Sherrer formula<sup>10</sup> using the half-maximum width of the (311) x-ray-diffraction line which broadens with decreasing crystallite size. The other was to use the BET method

which measures the surface area of the particles. If we know the bulk density and assume a particle shape, particle size can be calculated from the surface area. Even though the particle may not be perfectly spherical or cubic as we usually assumed, the size determined with this method may not differ too much from the real mean size provided that the surface is smooth and no pores exist inside the particle. In calculating the particle diameter  $d$ , a spherical particle shape was assumed and the bulk density of  $\text{MnFe}_2\text{O}_4$  (5.0 g/cm<sup>3</sup>) (Ref. 11) was used. The magnetic properties were measured with a VSM in the fields up to 17 kOe from room temperature to 450 °C. Ar gas flowed through the sample chamber during the thermomagnetic measurements.

## III. RESULTS AND DISCUSSION

X-ray diffraction showed that all samples after digestion were in a single  $\text{MnFe}_2\text{O}_4$  phase. Chemical analysis also revealed that the samples had the correct Mn/Fe ratio of 0.5. An important characteristic of our synthetic method was our ability to control particle size while keeping the stoichiometry and phase properties of the particles constant. In addition to the observation that the particle size depends on the pH value of the solution as in previous studies,<sup>2,3</sup> we have found that the diameter  $d$  was a unique function of the concentration ratio  $[\text{Me}]/[\text{OH}^-]$ , where  $[\text{Me}]$  was the total concentration of both metal ions  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$ . This ratio is a more definitive parameter than pH in that both the morphological and magnetic properties change considerably at  $[\text{Me}]/[\text{OH}^-] = 0.375$ , the stoichiometric ratio to produce  $\text{MnFe}_2\text{O}_4$ .<sup>9</sup> The diameter  $d$  increased roughly linearly from 5 to 25 nm as  $[\text{Me}]/[\text{OH}^-]$  varied from 0.05 to 0.3, while particle size decreased when  $[\text{Me}]/[\text{OH}^-]$  increased from 0.3 to 0.375. The particle sizes of these samples measured by the broadening of (311) x-ray-diffraction peak and by the BET method were in good agreement, indicating that the particles are single crystals. For  $[\text{Me}]/[\text{OH}^-] > 0.375$ , smaller multicrystallite particles were obtained. Our magnetic measurements were performed only on samples for which

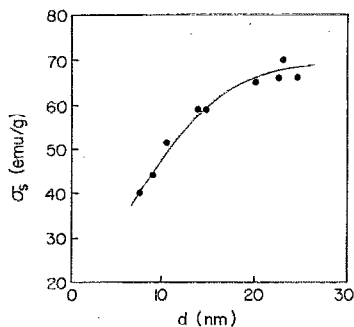


FIG. 1. Dependence of the saturation magnetization on the particle size.

$[Me]/[OH^-] < 0.3$ . The diameter  $d$  in this paper is from the BET measurement.

The relation between the saturation magnetization  $\sigma_s$  at room temperature and the particle size is shown in Fig. 1. Since  $MnFe_2O_4$  is very soft, it is not difficult to bring the samples to the saturation magnetized state even for the sample with  $d = 7.5$  nm. We calculated the  $\sigma_s$  simply as the magnetization value at  $H = 17$  kOe. The results in Fig. 1 are similar to that obtained earlier for the same ferrite in this size range.<sup>4</sup> The saturation magnetization for the bulk  $MnFe_2O_4$  at room temperature is 80 emu/g.<sup>11</sup> We found that  $\sigma_s$  is about 50% of the bulk value at  $d = 7.5$  nm and about 85% of the bulk value at  $d = 25$  nm, substantial decreases from the bulk value. Considering that the particles are single crystals, internal defects are not a likely contribution to this decreasing magnetization. Surface characteristics, described as a magnetically inactive layer or as the canting of the surface spins, probably cause this decreasing magnetization.

We measured the  $M$  vs  $T$  for samples of different size. Figure 2 shows the results of these thermomagnetic measurements and that for bulk Ni for comparison. The external magnetic field applied in these measurements was 700 Oe. The arrows in this figure indicate the transition temperatures. These temperatures were determined by the intercept of the extrapolations of the steepest slope below the transition and the base line after the transition. From this figure, we can see that (1) as the particle size decreases, the phase transition smears out over an increasing temperature

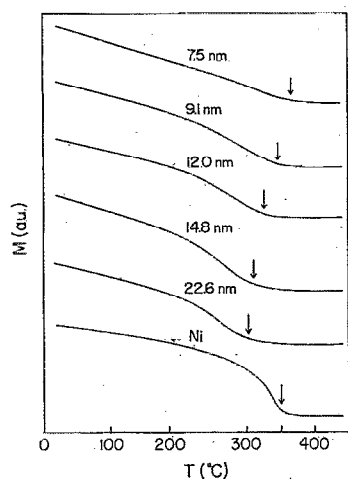


FIG. 2. Variation of magnetization ( $M$ ) with temperature for  $MnFe_2O_4$  fine particles. The numbers denote the particle sizes, and the arrows indicate the transition temperatures. The external magnetic field in these measurements was 700 Oe.

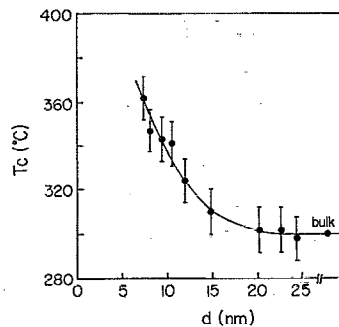


FIG. 3. Transition temperature vs particle size. The bulk Curie temperature of  $MnFe_2O_4$  is 300 °C (Ref. 11).

range. At  $d = 22.6$  nm, the curve below the transition temperature is clearly concave downward, while for  $d = 7.5$  nm that part of curve becomes almost a straight line. (2) The transition temperature changes with the particle size. For our smallest sample with  $d = 7.5$  nm, the transition temperature is  $361 \pm 10$  °C, 61 °C higher than that of the bulk  $MnFe_2O_4$  ( $T_c = 300$  °C).<sup>11</sup> Strictly speaking, this transition temperature is not the Curie temperature because of the finite size of the system even though we denote it as  $T_c$ .

We plot the transition temperatures as a function of the particle size  $d$  in Fig. 3. The size effect on the transition temperature is very obvious. When the particle size is larger than 20 nm, the transition temperature is the same as that of the bulk; no size effect is observed. When the particle size become smaller than 20 nm, the size effect starts to appear. The transition temperature increases as the particle size decreases.

It is important to know the effects of possible superparamagnetism in our small particles. Superparamagnetism, if present, would be dominant in our smallest particles; thus, isotherms were measured for the sample of the smallest size ( $d = 7.5$  nm). None of these isotherms collapsed to a single curve on a  $\sigma$ -vs- $H/T$  plot up to the transition temperature. This eliminates the possibility that our particles are noninteracting superparamagnetic with a single blocking temperature below the transition temperature. A mixture of ferrimagnetic and superparamagnetic states could be still possible, but this will not affect our conclusion of a size-dependent transition temperature. Since a superparamagnetic state will transform to the paramagnetic state at Curie temperature, a superparamagnetic state could only affect the  $M$ -vs- $T$  curvature, not the transition temperature. Therefore, the transition temperature, whether it is a pure ferrimagnetic state to paramagnetic state or a mixture of ferrimagnetic and superparamagnetic states to paramagnetic state, still shows the size effect.

We are not yet able to propose the reason for this size-dependent transition temperature. Valier *et al.*<sup>12</sup> have proposed a model involving a two-phase structure, the grain boundaries and bodies, to explain the decrease of the Curie temperature in submicrograined nickel. We observed an increase, however, and so such models involving inert heterogeneities would not seem to apply. On the other hand, finite-size scaling theory<sup>13</sup> predicts a size-dependent shift given by

$$[T_m(l) - T_c]/T_c \sim bl^{-\lambda},$$

where  $T_m(l)$  is the size-dependent transition temperature,  $T_c$  is the bulk Curie temperature,  $b$  is a constant,  $l$  is a measure of the size, and  $\lambda$  is the shift exponent. This functional form can describe our data. Other effects on the transition temperature which may show as an apparent size dependence include the effects of the surface magnetism of the particles, inhomogeneities in the particles, and possible extensive defects in the complex spinel-ferrite structure of the particles. Further work will be directed toward resolving the source of this effect.

#### IV. CONCLUSIONS

Single-crystal, stoichiometric manganese ferrite particles with controllable particle size have been created. The size was varied by changing the total metal ion to hydroxide ion concentration. The saturation magnetization, magnetic phase transition temperature, and nature of the transition were all found to be strong functions of the particle size for size less than 20 nm. Given the phase uniformity of our synthetic technique, these size dependencies may be of fundamental origin.

#### ACKNOWLEDGMENT

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