Magnetic coupling induced increase in the blocking temperature of γ-Fe_2O_3 nanoparticles

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In this article, we report the magnetic properties of surfactant coated γ-Fe_2O_3 nanoparticles which are pressed under different pressures. With increasing pressure, the sample volume decreases, density increases, and a 55% density change has been achieved. The blocking temperature is increased from 50 to 80 K. Analyzing the data of blocking temperature versus densities, which exhibits linear relationship, and comparing the magnetic properties, the increase in blocking temperature is understood in terms of increased magnetic interactions between neighboring nanoparticles, which is due to the reduced average interparticle distance by the applied pressure. © *2000 American Institute of Physics.* [S0021-8979(00)06410-0]

INTRODUCTION

Systems consisting of magnetic nanoparticles have been widely studied in recent years,[1–4] and their superparamagnetic properties have attracted much attention. The susceptibility as a function of temperature reveals some of the main features of a superparamagnetic system. It is well known that the thermal stability of the magnetic particles depends on the anisotropy of the particles, and it is also affected by the interparticle interactions. The blocking temperature T_B, below which the particle moments are blocked, is usually considered an important parameter when studying a magnetic nanoparticle system. In general, T_B can be obtained by analyzing the zero field cooled and field cooled (ZFC/FC) susceptibility versus temperature curve. The magnetic behavior of these particle systems has been explained by theoretical models based on the work of Néel,[5] Brown,[6] and Bean and Livingston.[7] In these models, one can use the treatment that the atomic magnetic moments within the particles are acting coherently and their magnetic moments can be represented by a single vector with a magnitude $\mu = N\mu_0$, where N is number of atoms in the particle and μ_0 is the average magnetic moment of an atom. Considering that the relaxation time τ is a function of temperature T and anisotropy barrier E_a,

$$\tau^{-1} = f_0 \exp(-E_a/k_B T), \tag{1}$$

where k_B is Boltzmann's constant, f_0 is a frequency factor on the order of $10^9\ s^{-1}$,[6] E_a is the anisotropy barrier that can be determined by $E_a = KV$ in which K is the anisotropy energy density constant, and V is the volume of particle.[8,9] The definition of blocking temperature of an ideal superparamagnetic particle system is given as follows:[10,8]

$$T_B = E_a/k_B \ln(tf_0), \tag{2}$$

where t is the experimental measuring time. $k_B \ln(tf_0)$ can be treated as a constant. Herein only the anisotropy energy barrier E_a has been considered. If we include the interaction between particles,[11,12] the energy barrier and blocking temperature will be modified

$$T_B = (E_a + E_{int})/k_B \ln(tf_0), \tag{3}$$

where E_{int} is introduced to indicate the interaction energy. Obviously higher interaction may cause higher T_B. The theoretical model of the interaction energy E_{int} has been introduced by Dormann *et al.*,[11,12] in which the interparticle interactions are treated as magnetic dipole–dipole interaction.

Samples containing magnetic nanoparticles (powder or bulk) can be made by several different ways: either chemical synthesis or physical methods like ball milling and film deposition. In an experiment, the blocking temperature T_B is normally determined by measuring the peak position of ZFC susceptibility versus temperature, the χ–T curve.[13,14] Often, the interactions between magnetic particles are ignored and the susceptibility data are analyzed without considering the interparticle distance or the density of particles. In reality these parameters influence strongly the interparticle magnetic interaction in the nanoparticle systems. We have designed an experiment to study how applied pressure and sample density affect the magnetic properties of a nanoparticle system, specifically how the blocking temperature is changed by compressing it.

EXPERIMENTS AND DISCUSSION

γ-Fe_2O_3 particles of spherical shape ranging from 6 to 7 nm in diameter were prepared using the method for the synthesis of magnetoliposomes. In this method, an aqueous ferrous solution was first trapped inside the phospholipid vesicles consist of dimyristoylphosphatidylcholine (DMPC) by direct injection. Ammonia solution was subsequently added to this system and its diffusion into the ferrous-containing vesicles causes the formation of nanosized par-

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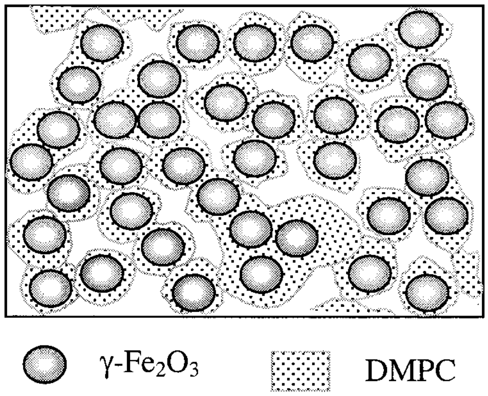

FIG. 1. The schematic view of $\gamma-Fe_2O_3$ nanoparticles surrounded by DMPC surfactant. The γ-Fe_2O_3 nanoparticles are well separated by the surfactant.

ticles of γ-Fe_2O_3 since those vesicles as nanoreactors restrict the growth of as-precipited particles within nanoscaled dimensions. Since there was no further purification, after drying, the γ-Fe_2O_3 particles were surrounded and isolated by the residual of DMPC surfactant. The thickness of the surfactant layer was estimated to be about 3 nm. Such a sample in which magnetic particles are embedded in a porous nonmagnetic matrix exhibits superparamagnetic behaviors; Figure 1 is the schematic view of this system. Particles are isolated from each other by the surrounding DMPC, and the system is compressible.

We used a steel die to apply the pressure on the bulk samples. Some nonmagnetic buffer powders have been used, which are separated from the samples by sample holders, to allow uniform pressure distribution. Both scotch tape and Cu foil have been used as the sample holders, and we found that there was no significant difference in experimental results when we used different sample holders. For each compression, we kept the pressure for 15 min to stabilize the volume change. By measuring the thickness of the compressed sample, the volume change of sample and its density were obtained. The susceptibility and magnetization measurements were made with a Quantum Design superconducting quantum interference device with temperatures varying from 5 to 300 K.

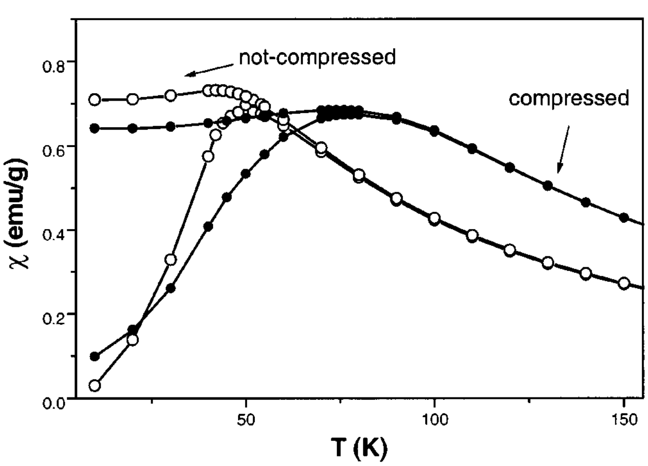

FIG. 2. ZFC and FC χ–T curves of γ-Fe_2O_3 samples before and after compressing. The blocking temperature T_B has been increased by ~ 28 K after the sample was compressed under pressure $P=5.0\times10^8$ N/m^2.

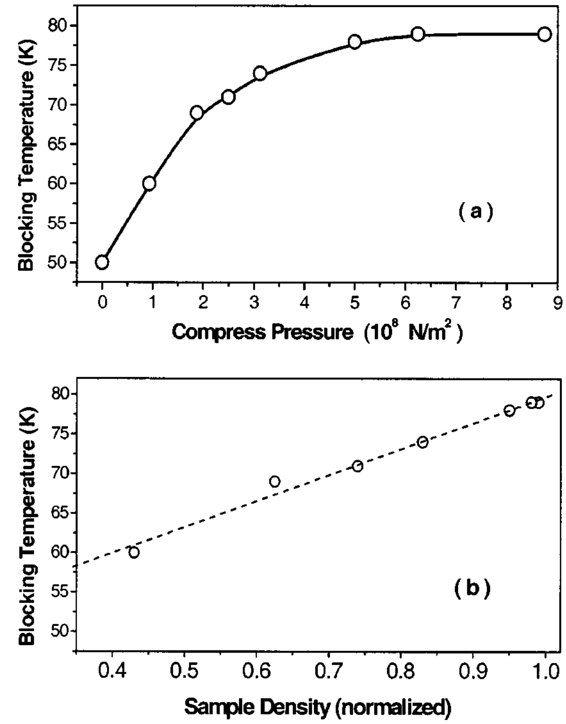

FIG. 3. (a) The blocking temperature T_B as a function of applied pressure. (b) T_B as a function of the sample density; a linear relationship between the T_B and density D exists.

Figure 2 illustrates that the susceptibility–temperature behavior of the system has been significantly changed after compressing under a pressure $P=5.0\times10^8$ N/m^2. The data were taken under both ZFC and FC conditions with an applied field of 50 Oe. Although no big change in the maximum value of the susceptibility after compression was found, the blocking temperature T_B has been increased significantly. It was enhanced by more then 50% after the sample was compressed under a pressure of 6.3×10^8 N/m^2. Figure 3(a) shows the pressure dependence of the blocking temperature T_B, and Fig. 3(b) shows the blocking temperature as a function of sample density. The blocking temperature T_B varies linearly with the density of the samples in the data range of our experiment.

To determine the causes of the increase in T_B, one may consider the changes in sample density, thus the interparticle distance and interaction, or the change in particle size, or the particle shape. As will be seen later, the change of interparticle distance is the main reason for the increase in T_B observed in our experiments.

We have compared the particle size before and after compression, which were measured by x-ray diffraction. The average particle size is about 6–7 nm in diameter and it was found that there was no significant change of the particle size after the samples had been compressed. The effect of pressure is essentially the densification of the porous DMPC matrix. With regard to the possible change of particle shape due to the pressure, the susceptibility and magnetization of the

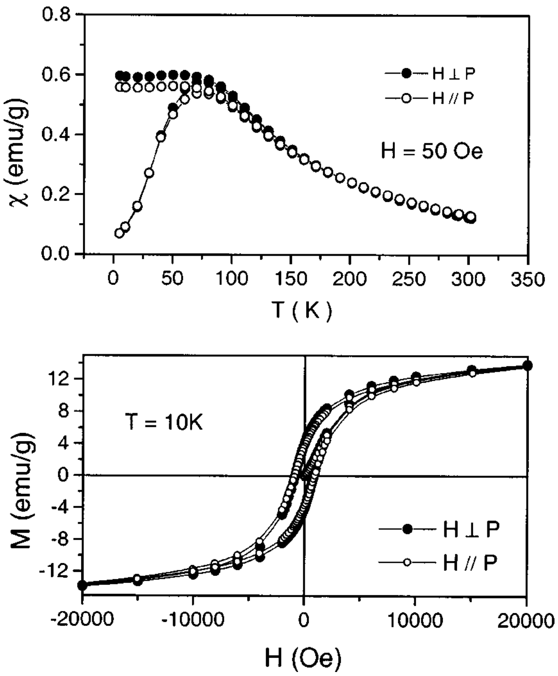

FIG. 4. The χ–T curves and magnetization curves of the pressed samples measured in two orientations. Open symbol corresponds to field parallel to the direction the pressure is applied, and solid symbol corresponds to field perpendicular to it.

compressed sample were measured in two different orientations: the applied field is parallel to the direction in which pressure was applied (**H**∥**P**), and perpendicular to it (**H**⊥**P**). As shown in Fig. 4, there is no difference in the susceptibilities and magnetizations between the two orientations. The coercivity measured at 10 K is also the same for the two orientations. This implies the γ-Fe_2O_3 particles do not change significantly from the spherical shape due to the applied pressure. So we are inclined to interpret the variation of T_B as being due to the change of sample density, that is, the change of particle distance, which affects the interparticle interaction. It should be pointed out that the γ-Fe_2O_3 nanoparticles are well separated by DMPC, and it is unlikely that the pressure can cause direct contact between neighboring particles and form a larger particle.

We consider the dipole–dipole interaction as the main coupling mechanism between magnetic particles. For two identical particles with magnetic moment M, interaction can be denoted as follows:[11,13,14]

$$E_{\mathrm{int}} \propto \frac{M^2}{r^3}(3\cos\psi_1\cos\psi_2 - \cos\alpha)\ , \tag{4}$$

where r is the distance between the particles, ψ_1 and ψ_2 are the angles between r and the two moments, respectively, and α is the angle between the two moments. Compressing changes the sample density and decreases the average distance r, which causes an increased interaction. According to Eq. (3), an enhanced T_B is expected. Considering that the density D is a function of particle distance r, $D \propto r^{-3}$, from Eqs. (2), (3), and (4) one can easily see the blocking temperature T_B is a linear function of the sample density D; that is $T_B \propto D$. This result agrees well with our experimental data shown in Fig. 3(b).

SUMMARY

In summary, we have studied a highly compressible system in which nanoparticles of γ-Fe_2O_3 are covered with a DMPC surfactant layer and well isolated from each other. The average interparticle distance can be controlled by applying a given pressure. The pressure reduces the interparticle distance, which leads to an increased magnetostatic interaction. With increasing coupling, the effective volume of the particles increases, and the blocking temperature T_B is greatly enhanced. The linear relationship found between T_B and sample density supports this explanation. Our results demonstrate the interactions between magnetic particles, which play an important role in the magnetic properties of superparamagnetic systems, and can be controlled by adjusting average particle distance through sample density in a properly chosen system.

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