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Surface-induced superparamagnetic relaxation in nanoscale ferrihydrite particles

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The effect of surface on superparamagnetic relaxation for nanoscale ferrihydrite particles ($d \sim 5$ nm) has been investigated using Mössbauer spectroscopy. With increasing surface chemisorption of SiO_4^{4-}, the superparamagnetic transition temperature (T_B) falls from 100 to 40 K and the transition sharpens. This indicates that the SiO_4^{4-} species eliminate the surface unpaired spins and create a nonmagnetic medium, thereby significantly reducing the magnetic coupling between the particles. For ferrihydrite particles impregnated on a silica support, the particle interaction becomes negligible and the superparamagnetic transition occurs at a still lower temperature of ~12 K; the spectra exhibit characteristic size-dependent features. [S0163-1829(96)02429-0]

INTRODUCTION

Magnetic nanoscale particles are single-domain particles. At temperatures below the Curie or Néel temperatures, while the magnetic moments of the individual atoms remain aligned, the magnetization vector of each particle fluctuates among the easy directions of magnetization. The phenomenon is known as superparamagnetism.[1] The superparamagnetic relaxation time is given by

$$\tau = \tau_0 \exp(KV/kT), \tag{1}$$

where k is the Boltzmann constant, τ_0 is of the order of 10^{-10}–10^{-13} s, K is the magnetic anisotropy energy, and V is the volume of the particle. KV represents the energy barrier between two easy magnetization directions.

^{57}Fe Mössbauer spectroscopy has been used extensively for the investigation of superparamagnetic relaxation in iron-based particles.[2] Above a certain temperature (the blocking temperature T_B), the time scale of Mössbauer spectroscopy, i.e., the Larmor precession time τ_L of the nuclear magnetic moment in the magnetic hyperfine field, is longer than τ and a paramagnetic quadrupole doublet spectrum is obtained. Below T_B, τ_L is shorter than τ and the spectrum exhibits magnetic hyperfine sextets. Near the blocking temperature T_B, because of a distribution of particle size, the typical Mössbauer spectrum usually consists of a paramagnetic doublet superimposed on a magnetic hyperfine sextet.

An unusual case is fine-particle goethite[3–5] (antiferromagnetic, $d = 10$–20 nm): its Mössbauer spectra exhibit magnetic sextets with broad absorption lines and reduced splittings at temperatures ranging from 200 to >300 K. The magnetic-paramagnetic transition occurs at $T > 300$ K, a value that appears to be higher than that estimated from the particle size and the anisotropy energy from the theory of superparamagnetism. The interpretation has been controversial. Mørup *et al.*[6,7] attributed the phenomenon to magnetic interactions among the particles and termed it ''superferromagnetism,'' to distinguish it from superparamagnetism for noninteracting particles. A modified Weiss mean-field theory was developed to fit the transition. On the other hand, Bocquet and co-workers[8,9] contended that the goethite particles are not superparamagnetic or superferromagnetic; rather, the Néel temperature is lower than that of well-crystallized goethite ($T_N = 393$ K) due to the presence of vacancy defects in the particles. Bocquet *et al.*'s conclusion is supported by neutron diffraction data.

Recently, we have extensively studied the structure, surface adsorption, and catalytic activity of ferrihydrite, an antiferromagnetic iron oxyhydroxide ($FeOOH \cdot nH_2O$) with average particle size of 3–5 nm. It is a naturally occurring mineral that can be found in iron-containing water, soil, river sediment, and oceanic crust.[10] Because of its small particle size and large surface area, the material has been developed as an absorbent and a catalyst for a number of applications. For the interest of physics, ferrihydrite is one of the smallest realizable magnets, which displays a variety of classical and quantum effects due to its nanoscale dimensions[11–15] (in the literature, ferrihydrite is often referred to as iron oxide–hydrate gel, amorphous FeOOH, etc.). Ferrihydrite is also related to ferritin, an iron reservoir in living organisms that consists of a ferrihydrite core of <10 nm diameter encapsulated in a protein shell of ~5 nm thickness.[16] By means of modern biological techniques, it is possible to manipulate the particle size and the magnetic state of ferrihydrite in ferritin because the confinement of the ferrihydrite core in the protein shell enables nanoparticles to be formed and stabilized that would otherwise not be possible.[17–19] These artificial ferritins provide an opportunity for a systematic study of superparamagnetic relaxation and quantum effects in nanoparticles.[19]

Using x-ray absorption fine-structure (XAFS) spectroscopy, we observed that,[20,21] although the iron atoms in the interior of ferrihydrite are octahedrally coordinated, as in goethite, a significant number of the surface iron atoms are coordinated by fewer than six O/OH ligands, and they become coordination unsaturated (CUS) after dehydroxylation. Upon exposure to moist air, the CUS sites readily adsorb water molecules to complete the coordination. These surface water molecules bond the small ferrihydrite particles into particle aggregates and, at elevated temperatures, the water molecules are evolved from the interparticle regions, promoting particle agglomeration and phase transformation to hematite (α-Fe_2O_3).[22] On the other hand, when impurity anions such as SiO_4^{4-}, PO_4^{3-}, MoO_4^{2-}, and anionic groups from organic acids are present during precipitation, the CUS

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sites may preferentially adsorb the impurity anions to form binary ferrihydrites (M/FHYD, M=Si, P, Mo, etc.).[21] The impurity anions are believed to be exclusively present at the surface because (1) the iron atoms within the ferrihydrite particles are octahedrally coordinated,[20,21] which precludes incorporation of tetrahedral-favoring Si, P, or Mo species in the interior; (2) the surface CUS sites are coordinated with reduced coordination (most likely tetrahedral),[20] which favors incorporation of the tetrahedral anions; (3) XAFS spectroscopy shows that the molybdate in Mo/FHYD has no significant coordination shell beyond its nearest oxygen shell, indicating that the Mo species are present at the surface, rather than substituting for Fe in the interior;[23] (4) there is significant retardation of phase transformation of binary ferrihydrites to crystalline goethite or hematite,[21] because the surface CUS sites are blocked by chemisorbed impurity anions; and (5) x-ray photoelectron spectroscopy (XPS) measurements for Si/FHYD show a decrease of Si concentration after Ar^+ ion sputtering, indicating that Si species are concentrated at the surface.[24]

The development of binary ferrihydrites provides a means of manipulating the surface by chemisorption of nonmagnetic species. For a 5 nm particle, about $\frac{1}{3}$ of the atoms are at the surface; therefore the magnetic properties of the ferrihydrite particles must be strongly dependent on the surface condition. In the following, we demonstrate that the presence of surface nonmagnetic species such as $SiO_4{}^{4-}$ reduces magnetic interaction between the ferrihydrite particles, resulting in a dramatic variation of their superparamagnetic relaxation behavior.

EXPERIMENTAL SECTION

Five samples were prepared. A pure ferrihydrite (FHYD) was synthesized by precipitation of a ferric nitrate solution with ammonium hydroxide. After filtration and washing, the sample cake was dried at 65 °C, ground into a fine powder, and vacuum dried at 130 °C. For ferrihydrites with chemisorbed $SiO_4{}^{4-}$ (Si_x/FHYD, with x=Si/Fe=0.05, 0.1, and 0.15), an appropriate amount of Na_2SiO_3 was added to the ferric nitrate solution before or after precipitation. The Si/Fe ratios for the samples are assumed to be the same as those in the precipitation solutions. Ferrihydrite impregnated on SiO_2 (FHYD/SiO_2) was prepared by mixing SiO_2 [Aldrich, Brunauer-Emmett-Teller (BET) surface area=500 m^2/g, pore volume=0.75 m^3/g] with a ferric nitrate solution. After the excess ferric nitrate solution was filtered out, the slurry was poured into ammonium hydroxide. Subsequently, the sample was washed repeatedly and vacuum dried at 90 °C.

X-ray diffraction (XRD) patterns of the ferrihydrites exhibit two very broad peaks (two-line ferrihydrite[10]) due to lack of crystallinity and small dimensions. Transmission electron microscopy (TEM) shows that the fine particles are heavily aggregated. However, for Si/FHYD, when the electron beam is focused on an aggregate, the particles can often be dispersed, suggesting relatively weak bonding between the particles. The average particle sizes estimated from TEM, are d=4 nm (FHYD), 5 nm ($Si_{0.05}$/FHYD), 5.7 nm ($Si_{0.1}$/FHYD), and 5.5 nm ($Si_{0.15}$/FHYD). The widths of the particle size distributions are ~1 nm.

Mössbauer spectra were recorded with a constant acceleration spectrometer. The radioactive source consists of ~50 mCi of ^{57}Co in a Pd matrix. Temperature-dependent measurements from 12 to 300 K were performed using an Air Products Displex refrigerator system. The temperature variation in the sample chamber is less than ±1.0 K.

RESULTS AND DISCUSSION

Mössbauer spectra recorded from the four ferrihydrites at temperatures from 12 to 100 K are shown in Fig. 1. At 12 K, all four samples exhibit a magnetic hyperfine sextet. The absorption lines are broad compared with those for crystalline goethite or hematite and indicate a distribution of magnetic field arising from the different atomic environments of the interior and the surface iron ions: the magnetic hyperfine fields at the nuclei of the surface iron ions are smaller than those in the particle interior.[25] The spectrum for FHYD at 12 K was least-square fitted with three sextets with magnetic hyperfine field H=507, 477, and 441 kG, isomer shift IS =0.52, 0.50, and 0.46 mm/s, and quadrupole splitting QS =0.05, 0.02, and 0.00 mm/s, respectively. The percentages of iron contributing to the three sextets are 44%, 38%, and 18% respectively. The interpretation of the parameters concerning the presence of tetrahedral sites has been previously addressed.[21]

For all the samples except $Si_{0.15}$/FHYD, as temperature increases, the magnitude of magnetic splitting decreases and the absorption lines broaden further, evolving into a complex V-shaped pattern, before finally collapsing to a paramagnetic doublet. Similar transition behavior for a pure ferrihydrite has been previously reported by Cianchi *et al.*[14] A comparatively sharp transition is observed in $Si_{0.15}$/FHYD without observation of a V-shaped spectrum. The spectra for the ferrihydrite impregnated on SiO_2 (FHYD/SiO_2) are quite different (Fig. 2) in that a well-resolved magnetic sextet is superimposed on a paramagnetic doublet at 12 K. Because of the low-temperature limitation of the refrigerator, we were unable to reach temperatures lower than 12 K. However, a completely magnetic spectrum is expected to appear at $T<12$ K for this sample.

As shown in Figs. 1 and 2, as temperature increases from 12 K, all samples undergo a superparamagnetic transition with varying transition temperature and width. The transition behavior of each sample can be followed by the variation of average magnetic hyperfine field, as represented by the magnitude of the magnetic splitting (MS), defined as

$$\mathrm{MS}=\sum_i I_i|V_i-V_0| \Big/ \sum_i I_i . \qquad (2)$$

In this equation, I_i is the intensity of the resonant absorption and V_i the velocity for channel i. The summation is taken over all 512 channels. MS values for the five ferrihydrite samples are plotted as a function of temperature in Fig. 3. The MS is further normalized, so that 1.0 represents the full magnetic splitting at 12 K and zero, the paramagnetic doublet. The superparamagnetic blocking temperature (T_B) is defined as the temperature at which MS→0. Figure 3 shows that with increasing Si/Fe ratio from zero to 0.15, T_B decreases consistently from 100 to 40 K. The transition also sharpens as a result of increasing Si/Fe ratio; whereas pure

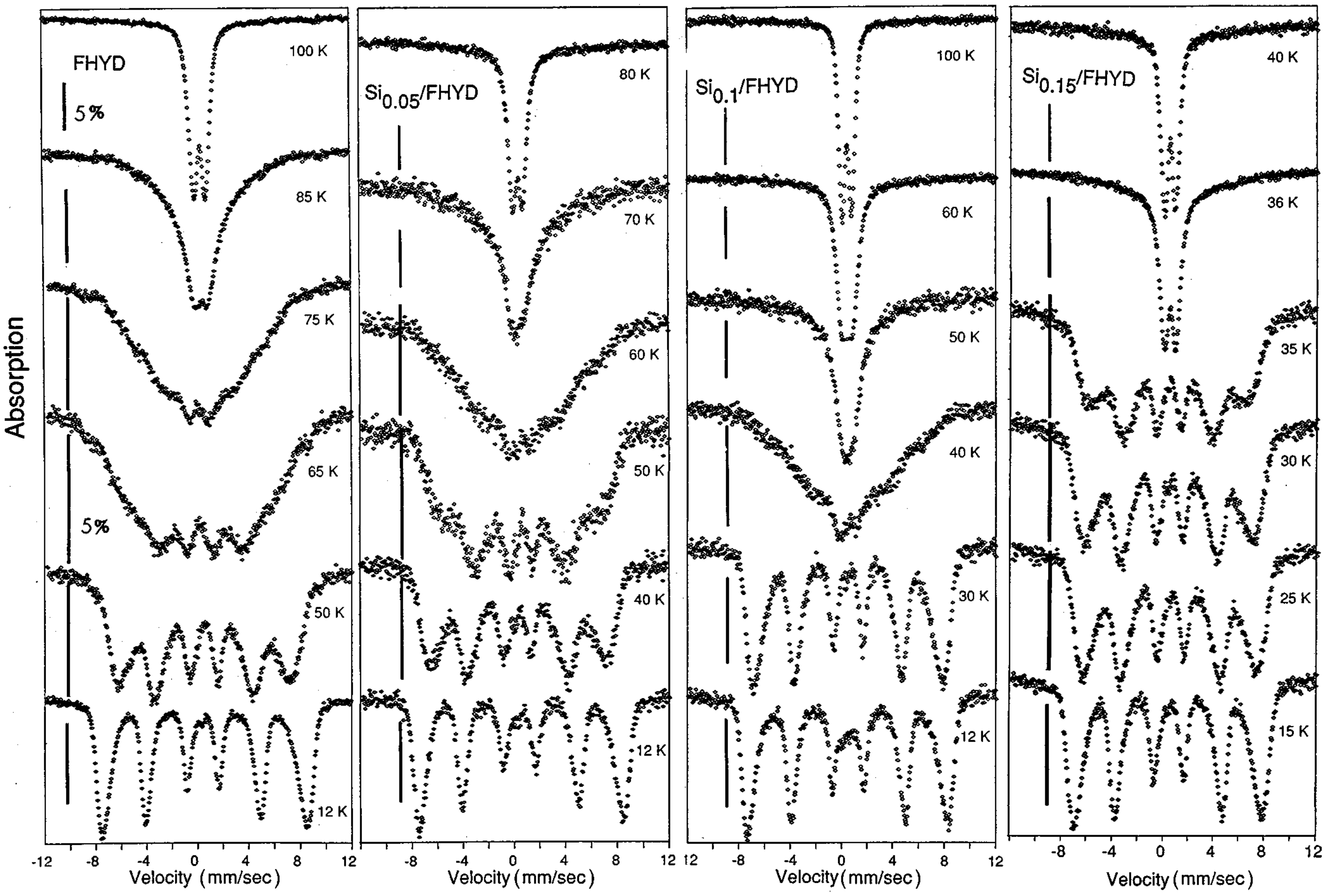

FIG. 1. Mössbauer spectra for FHYD and three Si/FHYD samples, recorded at various temperatures. The vertical bars on the left represent the scales of 5% absorption.

FHYD gradually evolves from a sextet to a doublet over a broad temperature range from 50 to 100 K, $Si_{0.15}$/FHYD undergoes an abrupt transition showing a resolved sextet at 35 K and a doublet at 36 K (Fig. 1). The decrease of T_B is certainly not caused by variation of particle size. In fact, as noted earlier, TEM indicates a slight increase of particle size for the Si/FHYD samples, which would be expected to result in an increase of relaxation time [Eq. (1)], i.e., higher T_B, if

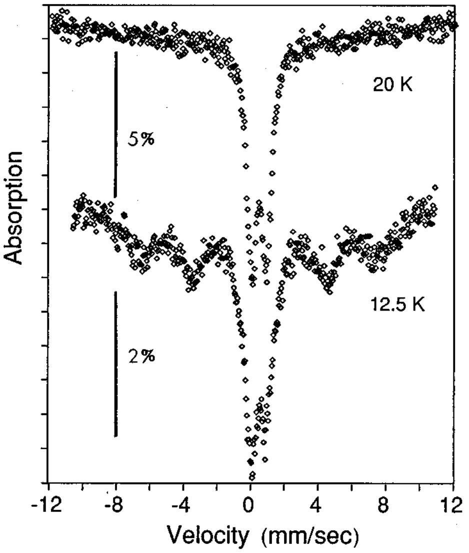

FIG. 2. Mössbauer spectra for FHYD/SiO_2 at 12 and 20 K. The vertical bars on the left indicate the scales of percentage absorption.

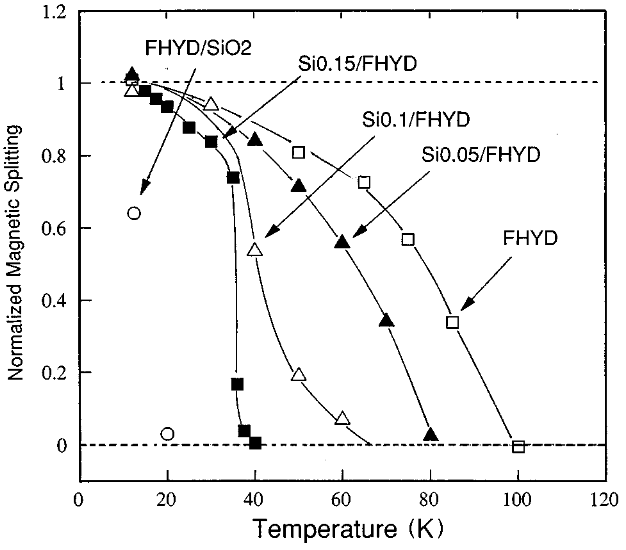

FIG. 3. Normalized magnetic splitting as a function of temperature for the ferrihydrite samples. Solid lines are drawn for visual purpose.

particle size were the dominant factor.

The above result agrees well with the superferromagnetic model. Mørup *et al.* proposed that for an assembly of interacting particles, the magnetic energy for particle i can be expressed as[6,7]

$$E_i = K_i V_i \sin^2\theta - \sum_j K^{ij} \mathbf{M}_i \cdot \mathbf{M}_j . \tag{3}$$

The first term represents the anisotropy energy of noninteracting particles or superparamagnetism, in which K_i is the magnetic anisotropy energy constant, V_i is the volume of particle i, and θ is the angle between the magnetic direction and an easy direction of magnetization. The second term represents the magnetic interaction energy or superferromagnetism, where K^{ij} is the magnetic coupling constant between particle i and its neighbor j, and $\mathbf{M}_i$ and $\mathbf{M}_j$ are the magnetization moments of particles i and j, respectively. The summation is taken over all jth neighboring particles.

For interacting particles, the magnetic energy could be dominated by the superferromagnetic term in Eq. (3). Magnetic interaction causes the magnetization vector of an individual particle to freeze: the stronger the magnetic interaction, the higher the temperature required to unfreeze the magnetization vector. The highest T_B is observed for pure FHYD, in which particles are in intimate interaction. Surface chemisorption of $SiO_4{}^{4-}$ creates a nonmagnetic medium between the particles and eliminates the surface unpaired spins from the same particle surface by allowing the electron charges to overlap, thus significantly reducing interparticle magnetic coupling and leading to a decrease in T_B. For FHYD/SiO_2, in which the ferrihydrite particles are dispersed into the pores of SiO_2, interparticle interaction is negligible; thus the superparamagnetic transition occurs at a much lower temperature of <12 K and the spectrum exhibits size-dependent superparamagnetism features. The transition behavior of FHYD/SiO_2 is similar to that for ferritin.[16] The ferrihydrite cores in ferritin are encapsulated in a thick protein shell (5 nm); therefore the magnetic interaction between the ferrihydrite cores is minimal. The spectra exhibit both sextet and doublet at $20 < T < 40$ K.[16] The average T_B for the ferritin sample is about 30 K, higher than that of FHYD/SiO_2 due to larger ferrihydrite core size (~8 nm).

For the interacting ferrihydrite particles with higher T_B, the V-shaped spectra at $T < T_B$ are attributed to the line broadening and increasing reduction of magnetic splittings as $T \rightarrow T_B$, and a distribution of the magnetic coupling constant K^{ij} [Eq. (3)]. These factors lead to a spectrum consisting of a paramagnetic doublet(s) superimposed on sextets with broadened absorption lines and varying magnetic splittings; that is, a V-shaped spectrum. At lower temperatures, the reduction of magnetic splitting is less; thus the transition becomes sharpened for samples with lower T_B, as in the cases of $Si_{0.1}$/FHYD and $Si_{0.15}$/FHYD. The sharp transition also suggests that there is a narrower distribution of K^{ij} for these two samples. In contrast, for noninteracting particles, the reduction of magnetic splitting as $T \rightarrow T_B$ is usually within 5–15 %.[7] Therefore, a distribution of particle size results in a spectrum with resolved sextet and doublet components, as in the cases of FHYD/SiO_2 (Fig. 2) and ferritin.[16]

The relaxation behaviors of fine-particle goethite (Figs. 4 and 5 in Ref. 6) are somewhat similar to that of the interacting ferrihydrite particles. However, Cianchi *et al.* argued that the Weiss mean-field theory by Mørup does not give a satisfactory fitting for ferrihydrite. Cianchi *et al.* interpreted the superferromagnetic spectra of ferrihydrite in terms of isotropic relaxation theory.[14,15] We have not yet tried to fit the spectra with a theoretical model at this time.

CONCLUSION

A simple procedure was developed to modify the surface of nanoscale ferrihydrite particles by chemisorption of $SiO_4{}^{4-}$. These Si species create a nonmagnetic medium in the interparticle region and eliminate surface unpaired spins, thus significantly reducing the magnetic interaction between the particles. A consistent decrease of superparamagnetic transition temperature with increasing Si content was observed. The technique also provides a semiquantitative probe to detect surface absorption in interacting nanoparticles, a subject that is of interest for colloid and catalysis science.

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