Temperature dependence of spontaneous magnetization of ultrafine Fe particles in Fe-SiO_2 granular solids

Gang Xiao and C. L. Chien
Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218

We have studied the temperature dependence of the spontaneous magnetization of ultrafine Fe particles by measuring the initial susceptibility $\chi \sim M_s^2(T)/k_B T$ in the superparamagnetic state. It was found that Bloch's law $M_s = M_0(1 - BT^{3/2})$ gives good description at temperatures much higher than the blocking temperature of the Fe particles. The value B is substantially larger than that of the bulk Fe, due to magnetic surface effect and finite size effect. Size distribution and magnetostatic interaction between particles have also been studied.

I. INTRODUCTION

Problems of fundamental interest in ultrafine ferromagnetic particles include the behaviors of spontaneous magnetization (M_s) and Curie temperature (T_C), and the effects of finite size and surface atoms. As the thermal energy surpasses the magnetic anisotropy energy of the particles, the moments of the particles fluctuate freely as if in a paramagnetic system with each particle bearing a giant moment. In such superparamagnetic state and particularly at temperatures much higher than the blocking temperature (T_B), saturation of the magnetic moments cannot be accomplished even with very large magnetic fields. Consequently, the temperature dependence of the spontaneous magnetization, Curie temperature, and other quantities of interest cannot be easily measured.

We have taken the advantage of superparamagnetism and measured the initial susceptibility $\chi \sim M_s^2/k_B T$ of the Fe-SiO_2 granular solids. The temperature dependence of $\sqrt{\chi T}$ provides a measure of the variation of the undisturbed spontaneous magnetization with temperature. Such technique has been used in several investigations[1] involving ultrafine Co, Ni, and γ-Fe_2O_3 particles. In these cases the temperature dependence of M_s closely follows that of the bulk materials. However, in the case of ultrafine Fe particles, large deviation has been found as described in this work.

II. EXPERIMENT

Magnetic granular Fe-SiO_2 films have been fabricated by using a rf magnetron sputtering system. The sputtering targets are homogeneous composite targets with chosen composition of Fe and SiO_2. The deposition was carried out at room temperature in a 4-mTorr pressure of Ar plasma. The presputtering background pressure was in the 10^{-8}–10^{-7} Torr range.

The samples used in this study are $Fe_{40}(SiO_2)_{60}$ (14 vol % of Fe) and $Fe_{50}(SiO_2)_{50}$ (21 vol % of Fe). The transmission electron microscopy (TEM) confirms the granular nature of the samples. The Mössbauer spectra of the samples at 4.2 K closely resemble those of the bulk Fe. A SQUID magnetometer with a field range of 0–50 kOe and a temperature variation of 2–400 K was used to study the magnetic properties.

III. RESULTS AND DISCUSSIONS

The particle size and its distribution are important parameters of an assembly of ultrafine ferromagnetic particles. In addition to microstructure characterizations, they can also be obtained by analyzing the magnetization curve $M(H)$ in the superparamagnetic state. The $M(H)$ of a noninteracting superparamagnetic system with uniform particle size is described by the Langevin equation

$$M = pM_s L\left(\frac{\mu H}{k_B T}\right) = pM_s\left[\coth\left(\frac{\mu H}{k_B T}\right) - \frac{k_B T}{\mu H}\right], \quad (1)$$

where p is the volume fraction of the magnetic particles, and $\mu(=M_s V)$ is the magnetic moment of a single particle with volume V. In all real systems, some size distribution is unavoidable. Therefore the obtained magnetization should be given by

$$M = pM_s \int_0^\infty L(V) f(V) dV, \quad (2)$$

where $L(V)$ is the Langevin equation and $f(V)$ the size distribution. It has been shown that the size distribution of ultrafine particle systems tends to have a tail towards large particle sizes.[2] Assuming spherical particles of diameter D for simplicity, the log-normal size distribution

$$f(D) = \frac{1}{\sqrt{2\pi}\ln\sigma} \exp\left(-\frac{(\ln D - \ln \overline{D})^2}{2(\ln\sigma)^2}\right) \quad (3)$$

gives an adequate description. Figure 1 shows the $M(H)$ of $Fe_{40}(SiO_2)_{60}$ and $Fe_{50}(SiO_2)_{50}$ measured at room temperature which is much higher than their blocking temperatures of $T_B = 12$ and 30 K. The log-normal size distribution provides an excellent description of the experimental data. The obtained values of $\overline{D}$, σ for $Fe_{40}(SiO_2)_{60}$ are 19 Å and 1.21, and for $Fe_{50}(SiO_2)_{50}$, 23 Å and 1.30.

As can be seen from Fig. 1, even at the highest field of 50 kOe, the magnetizations of the samples are still far from being saturated. Thus the saturation magnetization cannot be easily obtained with this conventional method. However, one can derive from Langevin equation (1) that at low fields the susceptibility is given by Curie's law:

$$\chi = \frac{M}{H} = \frac{pVM_s^2(T)}{3k_B T} \quad \text{for } \mu H < k_B T. \quad (4)$$

 0021-8979/87/083308-03$02.40

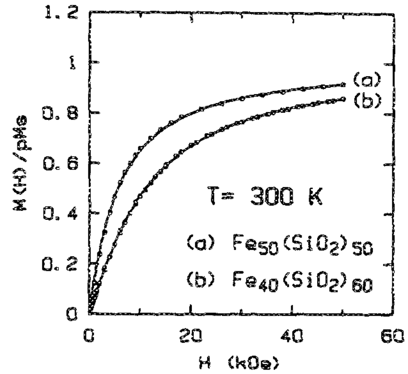

FIG. 1. Normalized magnetizations vs magnetic field at $T = 300$ K. The lines are theoretical magnetization curves obtained with log-normal size distribution. [$\overline{D} = 19$ Å, $\sigma = 1.21$ for $Fe_{40}(SiO_2)_{60}$ and $\overline{D} = 23$ Å, $\sigma = 1.30$ for $Fe_{50}(SiO_2)_{50}$.]

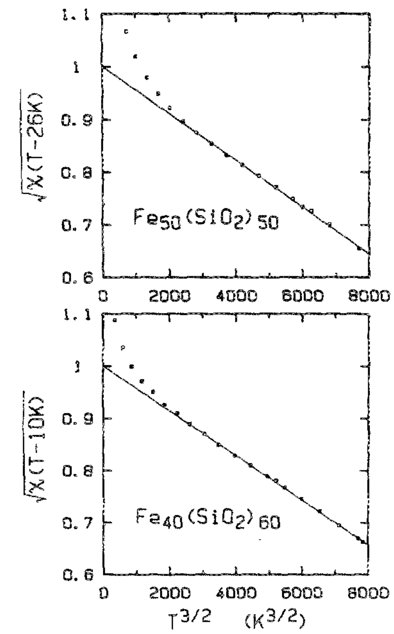

FIG. 3. $T^{3/2}$ dependence of $\sqrt{\chi(T - T_0)}$ that is proportional to $M_s(T)$. The spin-wave constant B is 4.30×10^{-5} for $Fe_{40}(SiO_2)_{60}$ and 4.46×10^{-5} for $Fe_{50}(SiO_2)_{50}$.

Therefore the temperature variation of $M_s(T)$ can be obtained by measuring the initial susceptibility (χ) as a function of temperature. A further advantage of this method is that as it is carried out at very low fields, the moments of the magnetic particles remain undisturbed.

The above discussions, which lead to Eq. (4), assume no magnetostatic interactions among the particles. In reality, especially at low temperatures where the relaxation of the moments is very slow, there are some spin correlations between particles. Chantrell and Wohlfarth[3] have investigated theoretically the interaction effect on the magnetic susceptibility of ultrafine particle systems. They found that χ can be described by a Curie–Weiss-like law

$$\chi \propto M_s^2(T)/(T - T_0) , \qquad (5)$$

where the parameter T_0 reflects the strength of the interactions. Monte Carlo calculations[4] and initial susceptibility measurement[5] also confirmed the Curie–Weiss-like behavior.

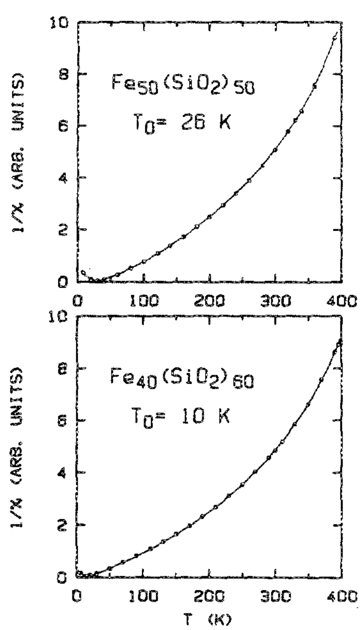

FIG. 2. Inverse susceptibilities vs temperature under a field of 5 Oe. The T_0 values were obtained from extrapolation.

We have measured the magnetic susceptibility of $Fe_{40}(SiO_2)_{60}$ and $Fe_{50}(SiO_2)_{50}$ at a field of 5 Oe in the temperature range of 5–400 K. The temperature dependence of $1/\chi$ of the samples is displayed in Fig. 2. Note that the data do not follow a straight line; this is because the magnetization of the particles is temperature dependent. As expected the curves do not intercept $T = 0$, indicating a Curie–Weiss-like behavior. The T_0 values obtained are about 10 and 26 K for $Fe_{40}(SiO_2)_{60}$ and $Fe_{50}(SiO_2)_{50}$, respectively.

Having obtained T_0 for the samples, we plot $\sqrt{\chi(T - T_0)}$, which is proportional to M_s of the ultrafine Fe particles, against $T^{3/2}$ in Fig. 3. At temperatures larger than 150 K, the data can be well described by straight lines, i.e., the M_s follows Bloch's law:

$$M_s(T) = M_0(1 - BT^{3/2}) . \qquad (6)$$

A noticeable departure from Eq. (6) at low temperatures where there is an enhancement of χ is observed. This is caused by the effect of size distribution. Even above the effective blocking temperature, some large particles at the tail of the particle distribution still remain magnetically blocked, which will generate a nonvanishing internal field and enhance the magnetic susceptibility. Equation (5) is valid only if all the particles are superparamagnetic.

The fact that $T^{3/2}$ dependence is observed indicates spin-wave excitations despite the small size of the ferromagnetic particles. However, the spin-wave constant B of the granular Fe particles are very different from that of the bulk Fe. The spin-wave constants B obtained from Fig. 3 are 4.30×10^{-5} $K^{2/3}$ and 4.46×10^{-5} $K^{2/3}$ for $Fe_{40}(SiO_2)_{60}$ and $Fe_{50}(SiO_2)_{50}$, respectively, considerably larger than the value of 3.3×10^{-6} $K^{2/3}$ for bulk Fe. There are several possibilities for the increase. Theories and experiments[6,7] on magnetic thin films have shown that the fluctuation of surface moments are larger than that of the interior moments so that the B constants for the surfaces are 2–3.5 times larger than that for the interior. In the case of ultrafine Fe particles with a diameter of 20 Å, the portion of surface atoms exceeds 50%, assuming that the surface layer consists of two atomic layers. Thus a large B value observed in Fe particles is, in part, a consequence of the abundance of magnetic surfaces. The other effect which may change the B constant is the finite size effect. It plays at least two roles in the magnetic properties of ultrafine particles. First, the physical properties such as spin-wave spectrum may be substantially altered from the bulk case, causing a softening of the spin waves. Second, the geometrical size causes a cutoff of the spin waves with wavelengths larger than the physical dimension of the particles. At this stage, there is a lack of theoretical and experimental studies on how the finite size effect affects the temperature dependence of M_s of ultrafine ferromagnetic particles. Further works are needed in this respect.

IV. CONCLUSIONS

The initial susceptibility of granular Fe-SiO_2 films as a function of temperature provides temperature dependence of the undisturbed spontaneous magnetization after considering the effects due to the magnetostatic interactions between particles. The M_s of the samples can be described by Bloch's law, with a substantially larger spin-wave constant B than that of the bulk Fe. Possible causes of such increase are magnetic surface effect and finite size effect.

ACKNOWLEDGMENT

This work is supported by Office of Naval Research Contract No. N0001485-K-0175.

[1] I. S. Jacobs and C. P. Bean, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. 3, p. 289, and references therein.
[2] C. G. Granqvist and R. A. Buhrman, J. Appl. Phys. **47**, 2200 (1976); Solid State Commun. **18**, 123 (1976).
[3] R. W. Chantrell and E. P. Wohlfarth, J. Magn. Magn. Mater. **40**, 1 (1983).
[4] S. Menear, A. Bradbury, and R. W. Chantrell, J. Magn. Magn. Mater. **39**, 17 (1983).
[5] K. O'Grady, A. Bradbury, S. W. Charles, S. Menear, J. Popplewell, and R. W. Chantrell, J. Magn. Magn. Mater. **31–34**, 958 (1983).
[6] D. L. Mills, Comments Solid State Phys. **4**, 28 (1971); Comments Solid State Phys. **4**, 95 (1972).
[7] D. T. Pierce, R. J. Celotta, J. Unguris, and H. C. Siegmann, Phys. Rev. B **26**, 2566 (1982).