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# Particle size dependence of the magnetic properties of ultrafine granular films

Sy_Hwang Liou
*University of Nebraska-Lincoln*, sliou@unl.edu

C.L. Chien
*The Johns Hopkins University, Baltimore, Maryland*

# Particle size dependence of the magnetic properties of ultrafine granular films

S. H. Liou[a] and C. L. Chien
*Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218*

Magnetic granular solids consist of ultrafine metal granules of nanometer sizes embedded in an insulating medium. The magnetic properties are dictated by the microstructure such as particle size, metal volume fraction, which are process controlled. We report the results of a series of granular $Fe_{60}(SiO_2)_{40}$ films in which the particle size has been systematically varied. The magnetic coercivity, ranging from 500 to 2200 Oe, increases with particle size. The ferromagnetic-superparamagnetic transition had been studied by SQUID magnetometry and Mössbauer spectroscopy. The value of the magnetic anisotropy energy is found to be much larger than that due to magnetocrystalline anisotropy.

## INTRODUCTION

Granular metal films are small metal particles of nanometer size embedded in an insulating matrix. The persistent interest in this class of composite material is due primarily to their unusual transport, optical, and superconducting properties.[1–3] The magnetic properties of granular Ni-($SiO_2$,$Al_2$,$O_3$), Co-$SiO_2$, Fe-$SiO_2$, etc.,[4–7] have also been reported.

The magnetic properties of granular solids are determined by the intrinsic properties and the volume fraction of the metal, as well as the granule size. The main features of the magnetic behavior of these films are the presence of a ferromagnetic-superparamagnetic transition and high coercivity.

The investigations of the granular films so far have been emphasized mostly on the properties affected by the metal volume fraction in the films. However, for a given process condition, the average size of the metal particles in granular films has been found also to depend on the metal volume fraction. This means that the physical properties discussed are affected by *both* the particle size and the volume fractions. There are very few systematic studies of the magnetic properties affected only by the different granular sizes.

In this paper we investigate the magnetic properties, and specifically, the particle size effects of granular $Fe_{60}(SiO_2)_{40}$, with a Fe volume fraction of $p = 0.29$. We have chosen the volume fraction of $p = 0.29$, which is much less than the percolation threshold ($p_c \simeq 0.6$), so that isolated granules can be assured. The magnetic properties have been found to depend sensitively on the particle size.

## EXPERIMENT

The granular metal films were made by using a high-rate magnetron sputtering device. The vacuum prior to sputtering was in the $10^{-8}$ Torr range with a $LN_2$ cold trap in the chamber. The granular metal film about 3–6 $\mu$m thick were prepared by rf sputtering at an argon pressure of $4\times10^{-3}$ Torr from composite targets of Fe and $SiO_2$. The composition of films, was determined by atomic absorption and fluorescence x-ray spectroscopy. The composition of the films were found to be very close to that of the sputtering targets (within 5 at. %). The microstructure of film was studied by transmission electron microscopy (TEM) and electron and x-ray diffractions. The magnetic properties were determined by SQUID magnetometry and Mössbauer spectroscopy.

## RESULTS AND DISCUSSIONS

The morphology of the composites was revealed by TEM. Figure 1 shows typical bright-field TEM images of $Fe_{60}(SiO_2)_{40}$ ($p = 0.29$) with different deposition conditions. By varying the substrate temperature from 300 to 875 K, the size of the granules increases from 30 to 50 Å. The ability to control particle size with a fixed metal volume fraction is clearly demonstrated by the data shown in Fig. 1. The particles are nearly equiaxial with small aspect ratios.

X-ray diffraction was used to examine the crystal struc-

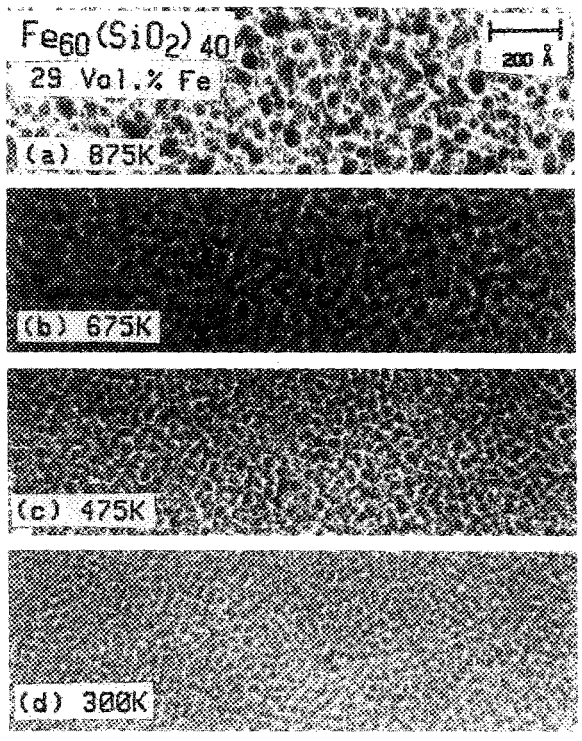


FIG. 1. TEM micrograph of granular $Fe_{60}(SiO_2)_{40}$ (29 vol. % Fe) films prepared at various substrate temperatures: (a) 875 K, (b) 675 K, (c) 475 K, (d) 300 K.

[a] Present address: AT&T Bell Laboratories, Murray Hill, NJ 07974.

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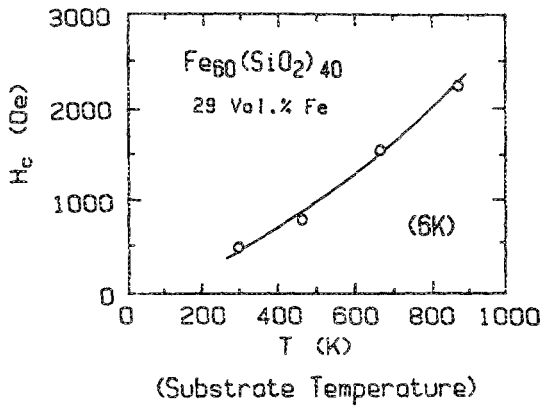


FIG. 2. Variation of coercivity of $Fe_{60}(SiO_2)_{40}$, 29 vol. % Fe, at 6 K with substrate temperatures.

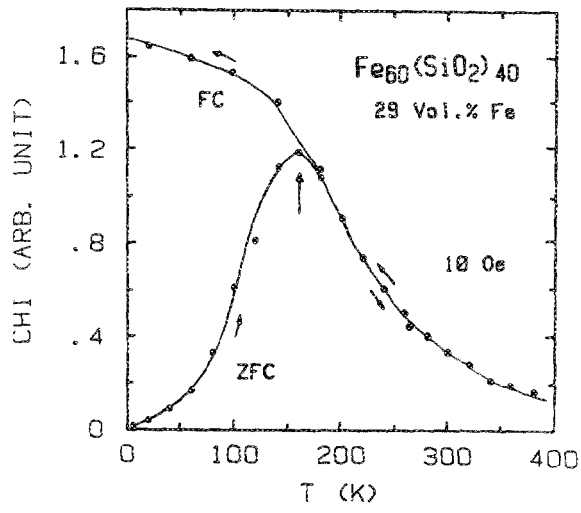


FIG. 3. Zero-field-cooled and field-cooled magnetic susceptibility vs temperature with an applied field of $H_a = 10$ Oe of $Fe_{60}(SiO_2)_{40}$ deposited at 675 K. The arrow indicates the blocking temperature of $T_{B1}$.

ture of the Fe particles. For the samples prepared at low substrate temperatures, the x-ray diffraction pattern of films can be consistently indexed to $\alpha$-Fe and the amorphous $SiO_2$ matrix. This is also confirmed by $Fe^{57}$ Mössbauer spectroscopy. However, there is an asymmetric broadening of the main x-ray diffraction peak, the (110) peak, suggesting the possibilities of other phases in the film. The asymmetric broadening is more pronounced for the film prepared at higher temperatures. The detail of this asymmetric broadening is still being investigated.

The magnetic coercivity ($H_c$) at 6 K versus the substrate temperature is shown in Fig. 2. The value of $H_c$ increases dramatically from 500 to 2200 Oe when the substrate temperature is increased from 300 to 875 K. Since higher substrate temperature produces larger granules, $H_c$ is evidently size dependent. For single domain small particles, there are a number of possible contributions (magnetocrystalline, shape, stress, surface, etc.) to $H_c$. In the case of Fe particles, the magnetocrystalline contribution, assuming it is the same as that of bulk Fe, is about 600 Oe, which is much smaller than the $H_c$ found in the films prepared at higher substrate temperatures. Effects due to stress, surface, and possibly long-range interaction between the particles cannot be easily delineated. Almost all the existing models of $H_c$ assume free-standing particles or particles dispersed in a nonbonding medium.[8] In granular Fe-$SiO_2$ films, the particles are strongly bonded to the matrix, probably under large stresses. A significant portion of the Fe atoms are also at or near the particle surface. Further investigations are needed to clarify the importance of these contributions.

Coercivity, remanence, and other magnetic properties of ultrafine single-domain magnetic particles decrease rapidly with temperature due to superparamagnetic relaxation. Assuming a simple Arrhenius law, the superparamagnetic relaxation time is[8]

$$\tau = \tau_0 \exp(CV/k_B T), \tag{1}$$

where $C$ is the total magnetic anisotropy energy per volume, $V$ is the particle volume, and $\tau_0$ is related to the natural gyromagnetic precession time, estimated to be in the range of $10^{-9}$–$10^{-13}$ s. Superparamagnetic behavior can be observed by using an instrument with a characteristic measuring time ($\tau_i$) and at temperatures above the blocking temperature ($T_{Bi}$), defined by

$$T_{Bi} = CV/k_B [\ln(\tau_i/\tau_0)] . \tag{2}$$

At $T > T_{Bi}$, the relaxation time of the magnetic moment vectors is shorter than $\tau_i$, hence the specimen appears to be paramagnetic even though each granule remains magnetically ordered. Superparamagnetism and the associated blocking phenomenon have been observed in magnetic granular materials by several techniques.[6,9,10] The two techniques we employed were SQUID magnetometry and $^{57}$Fe Mössbauer spectroscopy with characteristic times of $\tau_1 = 10$ s and $\tau_2 = 10^{-8}$ s, respectively. Such a large difference in characteristic times enables us to determine separately the relaxation time constant $\tau_0$, and the magnetic anisotropy energy ($CV$) of the granules. A significant advantage of using two measuring techniques is that the ratio of the measured blocking temperatures

$$T_{B1}/T_{B2} = \ln(\tau_2/\tau_0)/\ln(\tau_1/\tau_0) \tag{3}$$

is *independent* of sample. From Eq. (2), using the values of $\tau_1$, $\tau_2$, $T_{B1}$, and $T_{B2}$ one can obtain the magnetic anisotropy energy via

$$CV = k_B T_{B1} [\ln(\tau_2/\tau_1)/(1 - T_{B1}/T_{B2})] . \tag{4}$$

For the $Fe_{60}(SiO_2)_{40}$ sample deposited at 675 K, the magnetization under an applied field of 10 Oe is shown in Fig. 3, where the zero-field-cooled (ZFC) and field-cooled (FC) data are shown. $T_{B1} = 160$ K is chosen to be the cusp below which irreversible behavior is observed. The granular sample was then measured by $^{57}$Fe Mössbauer spectroscopy. At temperatures above the blocking temperature ($T_{B2}$), i.e., in the superparamagnetic regime, only a central peak was observed with no magnetic hyperfine splitting. At lower temperatures, magnetic hyperfine splitting appears, whose intensity increases at the expense of that of the central peak. The value of $T_{B2} = 450$ K can be conveniently determined using a zero-velocity thermal scan method, in which the in-

tensity of the central peak is measured as the sample temperature is varied. For other samples, of course the values of $T_{B1}$ and $T_{B2}$ will be different, but the ratio of $T_{B1}/T_{B2}$ remains the *same* at 0.35. It is clear from Eq. (4), since the terms within the brackets are independent of samples, $CV$ scales with the blocking temperature. The average diameter of the small particles obtained from TEM (Fig. 1) is 45 Å for $Fe_{60}(SiO_2)_{40}$ prepared at 675 K. Consequently the magnetic anisotropy constant ($C$) is $1.5\times10^7$ erg/cm$^3$. This value is about two orders of magnitude larger than bulk magnetocrystalline anisotropy of Fe ($1\times10^5$ erg/cm$^3$),[4] indicating that the magnetocrystalline anisotropy energy is not the main contribution in ultrafine single-domain particles.

In summary, we have synthesized Fe-$SiO_2$ granular films with different particle sizes by changing the substrate temperature. The much enhanced magnetic coercivity has been found to scale with the particle size. The ferromagnetic-superparamagnetic transition has been studied by both SQUID magnetometry and Mössbauer spectroscopy. From the measured blocking temperatures, whose ratio is found to be independent of samples, we have determined the magnetic anisotropy energy. The anisotropy constant is much larger than that due to magnetocrystalline anisotropy.

## ACKNOWLEDGMENT

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