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Magnetic relaxation in Fe-(SiO_2) granular films

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Magnetic relaxation of granular Fe-(SiO_2) solids with low metal-volume fraction has been studied by employing dc SQUID (superconducting quantum interference device) magnetometry and Mössbauer spectroscopy with the characteristic measuring time differing by nine orders of magnitude. The blocking temperatures (T_B), extrapolated to zero external field as measured by the two techniques maintain a constant ratio of 0.35 independent of samples. Arrhenius law was found adequate in describing the relaxation process, with a well-defined relaxation-time constant of $\tau_0 \simeq 10^{-13}$ sec. A cusp in the susceptibility is observed at T_B, below which irreversible difference between the field-cooled and zero-field-cooled magnetizations occurs. Despite this spin-glass-like behavior, granular magnetic systems are found to be fundamentally different from spin glasses.

The magnetic properties of granular materials have been a subject of extensive investigations and continuing interest because of their similarity with the spin-glass ordering.[1] For magnetically ordered materials, there exists a critical size, below which the granules can acquire only single magnetic domains even in zero applied field.[2] The critical size, for most materials, is of the order of a few hundred Å. At low temperatures ($T \simeq 0$ K), the magnetic-moment vectors of the isolated single-domain particles are randomly oriented and frozen, a situation similar to that of a spin-glass ordering. At elevated temperatures, the magnetic anisotropy energy barriers of the single-domain particles are overcome by thermal energy, and superparamagnetism occurs in which the magnetic vector of each particle is not fixed but fluctuates; i.e., all the moments in the single-domain particle rotate in unison. Since the magnetic anisotropy energy of an isolated particle is proportional to the volume of the particle, superparamagnetism is observed in ultrafine particles whose sizes are smaller than the critical size for a single magnetic domain. The superparamagnetic relaxation time is generally described by the Arrhenius law,[3] assuming that the interactions between particles are negligible

$$\tau = \tau_0 e^{CV/k_B T}, \quad (1)$$

where C is the magnetic anisotropy energy per unit volume, V is the volume, k_B is the Boltzmann constant, and T is the temperature. The value of τ_0, related to the natural frequency of gyromagnetic precession time, has been estimated to be in the range of 10^{-9} to 10^{-13} sec. The value of C includes anisotropy energy from several contributions: magnetocrystalline, shape, stress, and surface. Superparamagnetic behavior can be observed by using an instrument with a characteristic measuring time (τ_i) and at temperatures above the blocking temperature (T_{Bi}), which is defined by

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

At $T > T_{Bi}$, the relaxation time of the magnetic moment vectors is shorter than τ_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,[1,4] among them Mössbauer spectroscopy which has an attractive and well-defined characteristic time of about 10^{-8} sec.[5] However, if only one measuring time is employed, τ_0 and CV cannot be independently determined. Quite often a value of τ_0 (e.g., 10^{-10} sec) is assumed and the value of CV is then extracted. Independent determination of the magnetic anisotropy energy CV is rather difficult because of the many possible contributions and the lack of reliable calculations pertinent to the particular samples. The value of C in microcrystals can be orders of magnitude different from that of bulk specimens.[4] The actual value of τ_0 for the ultrafine particles assembly remains poorly known experimentally.

In this work, we report the observation of spin-glass-like characteristics and superparamagnetism using *two* measuring techniques with widely different characteristic times on carefully selected granular samples in which the blocking temperatures for *both* techniques can be easily measured. The two techniques we employed were SQUID magnetometry and ^{57}Fe Mössbauer spectroscopy with characteristic times of $\tau_1 \simeq 10$ sec and $\tau_2 \simeq 10^{-8}$ sec, respectively. Such a large difference in characteristic times enables us to determine separately the relaxation time constant τ_0, and the magnetic anisotropy energy of the granules. Measurements under very low fields (a few Oe), as provided by the SQUID magnetometer, are particularly advantageous for the determination of the magnetic properties of granular metal samples since a large applied field will drastically distort the relaxation process, making Eq. (1) invalid. Furthermore, by extrapolation from the results of the low-field measurements, the characteristics at zero applied field can be extracted. Mössbauer spec-

troscopy is administered without an applied field. Therefore, the two techniques that we have employed, both provide information under *zero* applied field for which Eq. (1) is defined. Finally, despite similar characteristics shared by magnetic granular solids and spin glasses,[1,6] we show that they are fundamentally different.

Because of the large difference between τ_1 and τ_2 in the two techniques, only small Fe granules of the order of a few tens of Å in size can be used as suitable samples in which blocking phenomena can be observed by both techniques within a convenient temperature range (2—500 K). The samples we have chosen are granular Fe-(SiO_2) solids, in which ultrafine Fe particles are embedded in a SiO_2 matrix. Our granular Fe-(SiO_2) samples have been fabricated through a high-rate sputter deposition process, either using homogeneous composite targets or by cosputtering, the details of which will be published elsewhere. The deposition temperature was either room temperature or 400 °C. The transmission electron microscopy (TEM) confirms the granular nature of the samples (Fig. 1). The relatively uniform shape and size are apparent and the electron diffraction measurements indicate that the granules are α-Fe. The amorphous SiO_2 matrix serves the purposes of protecting the Fe granules from oxidation as well as separating them. Since the percolation threshold, above which an infinite network of connecting granules is realized, occurs at about $x_p \sim 0.55$,[7] only samples with metal-volume fraction (x_V) much less than x_p consist of isolated granules. The samples $Fe_{50}(SiO_2)_{50}$ and $Fe_{60}(SiO_2)_{40}$ that we have used have volume fractions of 0.21 and 0.29, respectively. For samples with x_V considerably smaller or larger than this volume fraction range, the measurement of the blocking temperature by one of the two techniques becomes difficult.

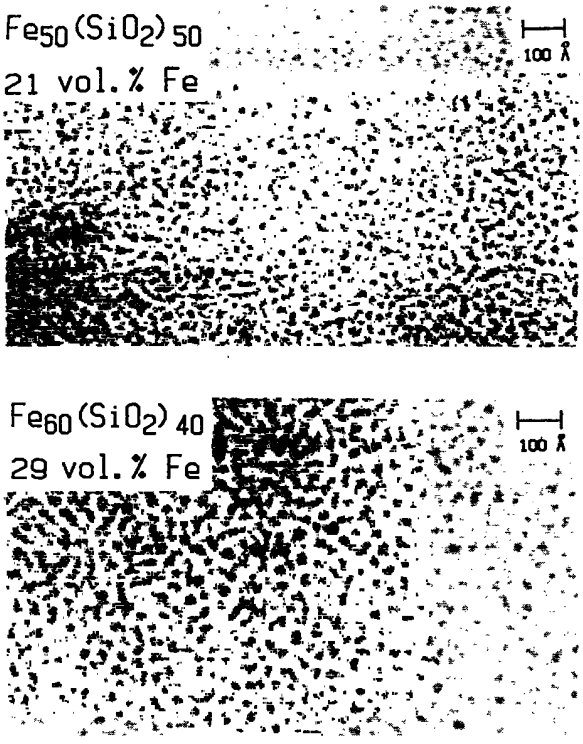

FIG. 1. TEM micrograph of granular $Fe_{50}(SiO_2)_{50}$ (21 vol. % Fe) and $Fe_{60}(SiO_2)_{40}$ (29 vol. % Fe) films.

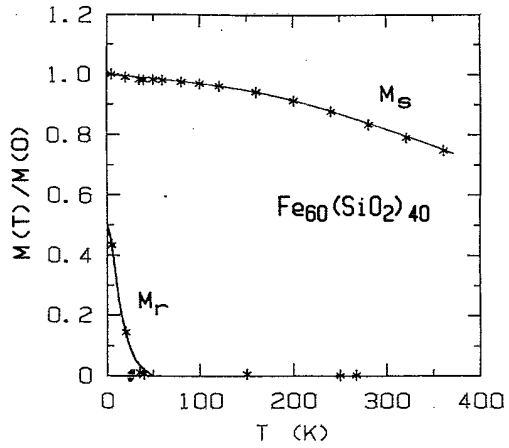

FIG. 2. Normalized magnetization at 50 kOe (M_s) and the remanence magnetization (M_r) of $Fe_{60}(SiO_2)_{40}$ as a function of temperature.

The saturation magnetization (M_s) under a large applied field (H_a) of 50 kOe, and the remanence (M_r) at $H_a = 0$ for $Fe_{60}(SiO_2)_{40}$ are shown in Fig. 2 as a function of temperature. The behavior of M_s is indicative of ferromagnetically ordered particles. The remanence, however, decreases rapidly with temperature and vanishes near the blocking temperature, indicating the onset of superparamagnetism. It should be noted that M_r at $T = 0$ K is about $\frac{1}{2}M_s$ for all these samples. This is because, after turning off the saturation field, the remanence is measured from the sample in which the magnetic vectors are randomly oriented only in the hemisphere, and hence

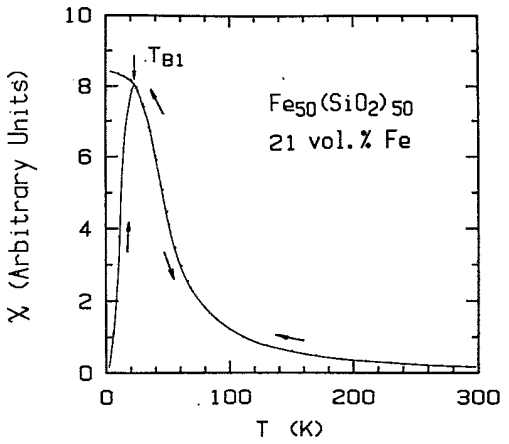

FIG. 3. Typical zero-field-cooled and field-cooled magnetic susceptibility vs temperature curve with an applied field of $H_a = 50$ Oe.

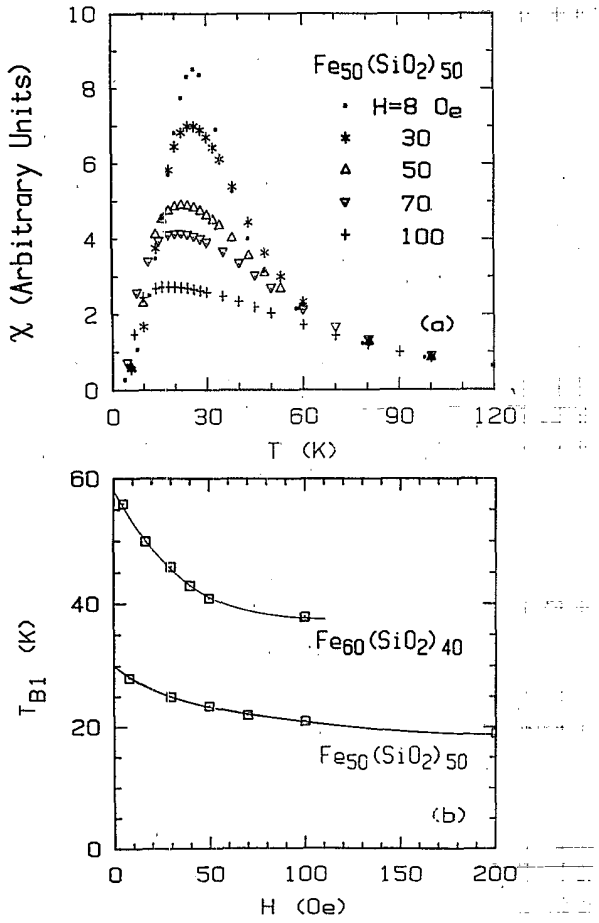

FIG. 4. (a) Temperature dependence of magnetic susceptibility of $Fe_{50}(SiO_2)_{50}$ at different magnetic fields. (b) Effective blocking temperature T_{B1} as a function of external magnetic field. The zero field T_{B1} is obtained from the extrapolation to $H_a=0$.

$\langle\cos\theta\rangle=\frac{1}{2}$. In fact $M_r=\frac{1}{2}M_s$ at $T=0$ K is an experimental signature expected for all samples with well-separated ultrafine particles and randomly distributed magnetic easy axes.[8]

The magnetization of $Fe_{50}(SiO_2)_{50}$ under $H_a=50$ Oe is shown in Fig. 3, where the zero-field-cooled (ZFC) and field-cooled (FC) data are shown. In the ZFC operation, the sample was cooled in $H_a=0$ to 6 K and the measurements were taken under $H_a=50$ Oe. In the FC operation, the samples were measured in $H_a=50$ Oe during cooling. It is evident that above T_{B1}, the FC and the ZFC data are the same and reversible. Below T_{B1}, the ZFC and FC data are totally different. The cusplike behavior of the ZFC data, and the difference between FC and ZFC are very similar to those found in the spin-glass state.

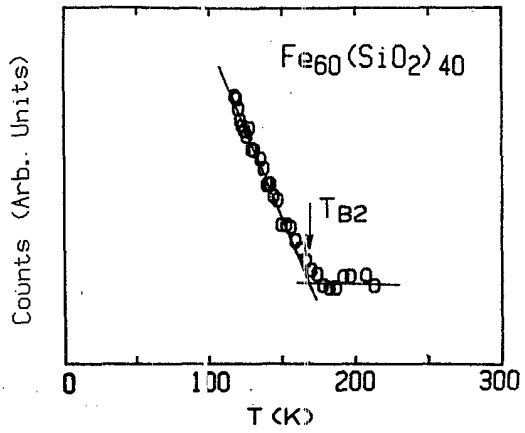

FIG. 5. Zero-velocity Mössbauer thermal scan of a $Fe_{60}(SiO_2)_{40}$ sample deposited at room temperature. The arrow indicates the blocking temperature T_{B2}.

We then investigated the expected significance of H_a by measuring ZFC magnetization for a number of H_a. The resulting susceptibility $\chi=M/H_a$ is shown in Fig. 4(a). Significant distortion occurred for $H_a \gtrsim 30$ Oe; above 100 Oe the susceptibility peak was distorted beyond recognition, illustrating the importance of measurements using low H_a. If one takes the maximum of each curve as the effective blocking temperature, the effects of H_a are shown in Fig. 4(b). Only under $H_a \lesssim 10$ Oe can one obtain blocking temperatures which are essentially that of $H_a=0$. Blocking temperatures (T_{B1}), extrapolated to $H_a=0$, are listed in Table I.

These granular samples were 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} can be conveniently determined using a zero-velocity thermal scan method, in which the intensity of the central peak is measured as the sample temperature is varied (Fig. 5). The values of T_{B2}, which are very *different* from T_{B1}, are listed in Table I.

One obtains from Eq. (2)

TABLE I. Deposition temperatures, blocking temperatures obtained from SQUID (T_{B1}), Mössbauer (T_{B2}), and the ratio T_{B1}/T_{B2} for various granular samples.

Sample	Deposition temperature (K)	SQUID T_{B1} (K)	Mössbauer T_{B2} (K)	Ratio T_{B1}/T_{B2}
$Fe_{50}(SiO_2)_{50}$	300	30	86	0.349
$Fe_{60}(SiO_2)_{40}$	300	58	167	0.347
$Fe_{60}(SiO_2)_{40}$	670	158	448	0.353
Co-sputtered Fe-(SiO_2)	300	44	123	0.358

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

which is *independent* of the sample. Equation (3) can be rewritten as

$$\tau_0=\tau_1^{1/[1-(T_{B2}/T_{B1})]}\tau_2^{1/[1-(T_{B1}/T_{B2})]}\ . \tag{4}$$

One notes from Table I that the same ratio of about $T_{B1}/T_{B2}\simeq 0.35$ has been obtained for *all* granular samples, indicating that τ_0 is essentially *independent* of samples. Using $\tau_1\simeq 10$ sec, $\tau_2\simeq 10^{-8}$ sec, and $T_{B1}/T_{B2}\simeq 0.35$, one obtains $\tau_0\simeq 1.4\times 10^{-13}$ sec. This is a physically reasonable value. There have been claims[1] that Arrhenius law cannot adequately describe the magnetic relaxation process in magnetic granular systems, because the obtained τ_0 value is too small (10^{-18} s). In our study, the fact that T_{B1}/T_{B2} remains essentially the same for different samples and an adequate τ_0 (10^{-13} s) value is obtained indicate that the Arrhenius law remains intact.

From Eq. (2) we can obtain the magnetic anisotropy energy

$$CV=k_B T_{B1}[\ln(\tau_1/\tau_2)/(1-T_{B1}/T_{B2})]\ . \tag{5}$$

Since the term inside the bracket is a constant, CV thus scales with the blocking temperature. The average diameters of the small particles obtained from TEM (Fig. 1) are 25 and 38 Å for $Fe_{50}(SiO_2)_{50}$ and $Fe_{60}(SiO_2)_{40}$, respectively. Consequently the magnetic anisotropy constants C are 1.7×10^7 and 8.8×10^6 erg/cm^3. These values are about two orders of magnitude larger than bulk magnetocrystalline anisotropy of Fe (1×10^5 erg/cm^3),[4] indicating that the magnetocrystalline anisotropy energy is not the main contribution in single-domain particles. Another point of interest is that the magnetic anisotropy constant of small particles is very sensitive to particle size, implying a large contribution from the stress anisotropy and surface anisotropy of the surface atoms. The smaller the particle size, the larger the fraction of surface atoms, therefore the magnetic anisotropy constant should increase with decreasing particle size. This is confirmed by our experimental data.

In all real systems of granular metal films, there are unavoidable distributions of granule sizes, corresponding to a distribution of blocking temperatures. However, theoretical calculations[9] indicate that, even for a rather wide particle distribution, there exists a *single* effective $T_B^*=bT_B$ at which a susceptibility maximum occurs. The value of b depends on the exact form of the distribution. But the precise value of b does not influence the determination of τ_0 since it is canceled out in Eq. (3).

The fact that the blocking temperatures obtained from SQUID magnetometry and Mössbauer spectroscopy are drastically different from each other while maintaining a constant ratio indicates clearly that the transition from the blocked state to the superparamagnetic state is not a phase transition but merely a relaxation effect. A magnetic granular system, therefore, does not exhibit a phase transition at finite temperature.

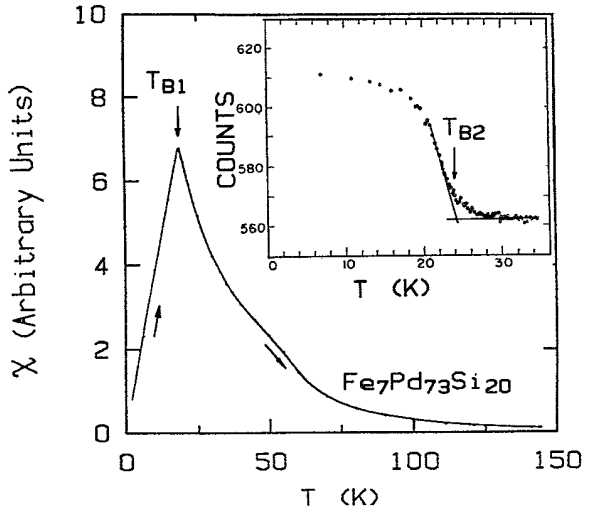

FIG. 6. Magnetic susceptibility of spin-glass $Fe_7Pd_{73}Si_{20}$ vs temperature at $H_a=7$ Oe. Insert: zero-velocity Mössbauer scan of $Fe_7Pd_{73}Si_{20}$.

The nature of the elusive spin-glass state remains controversial. On the one hand, the passage from paramagnetism to the spin-glass phase has been described in terms of a broad spectrum of relaxation times which are presumably due to the formation of magnetic clusters,[10] a situation not unlike that of granular magnetic systems. Any apparent transition would only result from finite measuring times. On the other hand, the spin-glass state is considered to be a phase transition at $T=T_{SG}$.[11] However, it remains difficult experimentally to unequivocally determine the validity of either of these models as demonstrated by recent experiments[12] and theories[13] on critical lines predicted by the models. In order to compare granular magnetic systems with spin glasses, we have applied the same techniques to amorphous $Fe_7Pd_{73}Si_{20}$, a well-known spin glass.[14] Figure 6 shows the low-field susceptibility and the Mössbauer scan. The T_{SG} temperatures determined from the two techniques are rather close at $T_{SG1}=19$ K and $T_{SG2}=24$ K. Arrhenius law is obviously inadequate here because τ_0 would be unphysically small (10^{-50} s). As a matter of fact, Arrhenius law has been found unable to account for the relaxation behavior in a number of spin-glass systems such as $Eu_xSr_{100-x}S$,[12,15] *Al*Gd,[12] etc. However, the phenomenological Vogel-Fulcher law $\tau=\tau_0\exp[E_a/k_B(T-T_0)]$ gives a good description,[12] the relaxation time shows a sharp increase near T_0 which might signal a transition, and τ_0 is of the order of 10^{-13} sec. In $Fe_7Pd_{73}Si_{20}$, T_0 thus obtained is 17.5 K. Therefore, despite some similar experimental signatures, granular systems and spin glasses are fundamentally different.

In conclusion, by employing SQUID magnetometry and Mössbauer spectroscopy with widely different measuring times, we have determined the relaxation time constant

(τ_0) and the magnetic anisotropy constant C of granular Fe-(SiO_2) system. Large differences in blocking temperatures but with the same ratio are found for different measuring times as predicted for superparamagnetic systems. Arrhenius law remains intact in our system. These phenomena are distinctively different from those of a spin glass.

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