Low Temperature Surface Spin-Glass Transition in γ-Fe_2O_3 Nanoparticles

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γ-Fe_2O_3 magnetic nanoparticles, with a very high surface to volume ratio, exhibit both strong exchange anisotropy and magnetic training effect. At the same time high field irreversibility in $M(H)$ curves and zero field cooled–field cooled (ZFC-FC) processes has also been detected. A low temperature spin-glass-like transition is evidenced at $T_F \approx 42$ K with strong irreversibility even at $H =$ 55 kOe. $T_F(H)$ evolves following the well known de Almeida–Thouless line $\delta T_F \propto H^{2/3}$. The thermal dependence of the exchange anisotropy field H_E is described by the random-field model of exchange anisotropy. In the framework of this theory, a surface spin-glass layer about 0.6 nm thick is determined. [S0031-9007(97)04941-7]

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Magnetic nanoparticles are a subject of intense research due to their unique magnetic properties which make them very appealing from both the theoretical and the technological points of view [1]. Below a critical size, magnetic particles become single domain in contrast with the usual multidomain structure of the bulk magnetic materials and exhibit unique phenomena such as superparamagnetism [2,3], quantum tunneling of the magnetization [4], and unusual large coercivities [5].

One of the most controversial issues in magnetic nanoparticles is the observed reduction of the saturation magnetization M_S, pointed out in the late sixties by Berkowitz and co-workers [6]. A random canting of the particles' surface spins caused by competing antiferromagnetic exchange interactions at the surface was proposed by Coey [7] to explain this reduction. Since then, the problem has been revisited several times [8–11] with arguments in favor of a surface origin [8,9] and in favor of a finite size effect [10,11], but no clear conclusions about the problem have been given yet. Recently, polarized neutron scattering in $CoFe_2O_4$ [12] and Mössbauer and magnetic experiments in $NiFe_2O_4$ [13,14] point to surface spin disorder as the origin of this reduction. Based on these results, a model of a ferrimagnetic core surrounded by a surface layer of canted spins has been proposed for $NiFe_2O_4$ particles and its implications on the macroscopic quantum tunneling carefully analyzed [14].

In this Letter, we demonstrate the existence of a spin-glass-like surface layer that undergoes a magnetic transition to a frozen state below $T_F \approx 42$ K. The existence of this spin-glass phase is evidence by the field dependence of T_F following the de Almeida–Thouless (AT) line $\delta T_F \propto H^{2/3}$ [15] that signals the starting point of the many-valley structure of phase space leading to diverging relaxation times and to nonergodic behavior.

γ-Fe_2O_3 nanoparticles have been fabricated by a vaporization-condensation process in a solar image furnace [16]. The particles obtained in this way have a very clean surface free of any kind of secondary products. The purity of the obtained vapor-condensed powders has been tested using x-ray diffraction, electron diffraction [17], and Mössbauer spectroscopy [18]. The nanoparticles are almost perfect single crystals exhibiting isotropic platelet shapes with mean sizes around 9–10 nm with aspect ratio $D/t \approx 4$, which gives a very large specific surface area. Magnetization measurements were carried out by using a commercial SQUID magnetometer in the temperature range from 5 to 300 K and in applied magnetic fields up to 55 kOe.

Low field zero field cooled–field cooled (ZFC-FC) magnetization curves exhibit the typical blocking process of an assembly of superparamagnetic particles with a distribution of blocking temperatures (see Fig. 1) at $T_B \approx$ 72 K. Nevertheless, a careful analysis of the FC branch clearly reveals the existence of a sudden increase of the magnetization below about 42 K (inset of Fig. 1) related, as we will see later, with the onset of the freezing process

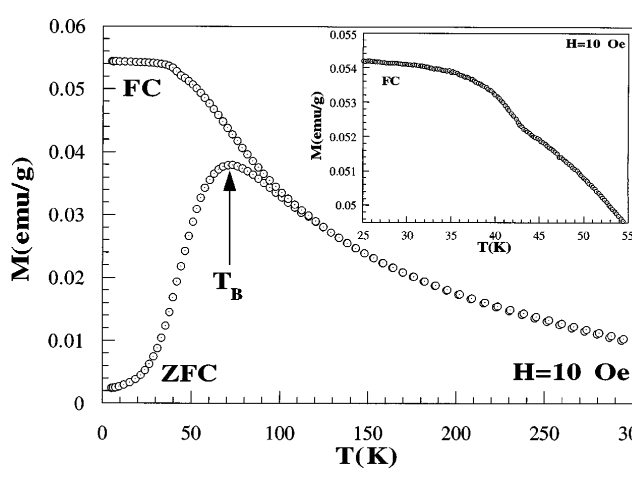

FIG. 1. Low field ZFC-FC magnetization of the γ-Fe_2O_3 nanoparticles showing the blocking process of the particles at $T_B \approx 75$ K. Inset: Detail of the FC branch showing the sudden increase of the magnetization at about 42 K.

of the surface spin-glass layer. It is expected that the strong irreversibility associated with the blocking process of the magnetic particles should disappear for applied fields of a few kOe when the anisotropy field of the particles is surpassed and particles are supposed to be saturated. Nevertheless, irreversibility remains below about 42 K up to the highest field used ($H = 55$ kOe) in both $M(H)$ and ZFC-FC processes (Fig. 2), together with an extremely low value of $M_S \approx 5$ emu/g at 5 K [15 times smaller than the saturation magnetization of γ-Fe_2O_3 bulk material (80 emu/g) [7]]. It is worth mentioning here that both M_S and high field irreversibility (HFI) are strongly dependent on the particle size and for particles of about 200 Å; the former reaches the bulk value (80 emu/g) while the latter has completely disappeared.

It is found that the temperature T_F at which the irreversible magnetization, defined as $\Delta M = M_{FC} - M_{ZFC}$, becomes different from zero, indicating the onset of the freezing process, decreases as H increases following a power dependence below about 40 K, namely, $\delta T_F \propto H^{2/3}$ (see Fig. 3). This dependence corresponds to the so-called AT line given by [15]

$$H_{AT}(T)/\Delta J \propto (1 - T/T_F)^{3/2}. \qquad (1)$$

The extrapolation of the AT line back to $H = 0$ gives the spin-glass transition temperature $T_F \approx 42$ K, which is in perfect agreement with the observed increase of $M(T)$ at low field (inset of Fig. 1) and the appearance of the exchange anisotropy field H_E. Even though the process is very akin to that observed in spin glasses, it should be kept in mind that, in this case, the field is very high (55 kOe) when compared with those typically used in spin glasses (few tens of Oe). This strong change of fields clearly establishes the different scale of energies relevant in each case and points to the direct competition of exchange interactions between surface spins as the origin of the high field irreversibility.

If spin disorder exists in the whole volume of the particle, a reentrant spin-glass behavior should be expected. In such conditions, increasing the magnetic field should favor the ordered state and T_F should move to lower T following a power law given by $\delta T_F \propto H^{1/2}$ [15]. The very similar field dependence of δT_F in this case with the AT line makes it difficult to decide whether or not the system behaves as a reentrant spin glass. Nevertheless, in reentrant systems, the low temperature spin-glass phase is very sensitive to the field and the application of fields of several orders of magnitude smaller than $k_B T_F/\mu_B \approx 6 \times 10^5$ G makes it disappear [15]. In our case, this is not true and the spin-glass phase remains up to the highest field used, behavior that points to the fact that the ferrimagnetic (FM) core and the spin-glass surface layer are well defined; in other words, magnetic disorder is confined in a well delimited surface layer. High field relaxation processes in alternating fields, after a ZFC process [14], give further support to this model (inset of Fig. 3), namely, a FM core that changes its orientation by coherent rotation plus a surface spin-glass layer that slowly relaxes in the direction of the field. The origin of this spin-glass-like phase at the surface may be the existence of broken bounds and the translational symmetry breaking of the lattice, generating randomness in the exchange interactions that extends to some atomic layers from the surface.

The observation of shifted hysteresis loops and strong magnetic training effect (see Figs. 2 and 4), after cooling the sample in a high field through the freezing temperature T_F, clearly reinforces this model. The field offset from the origin is the so-called exchange anisotropy field, H_E [19]. In the FC process, a preferred orientation is imposed upon the spin-glass-like surface spins, while the FM core, with

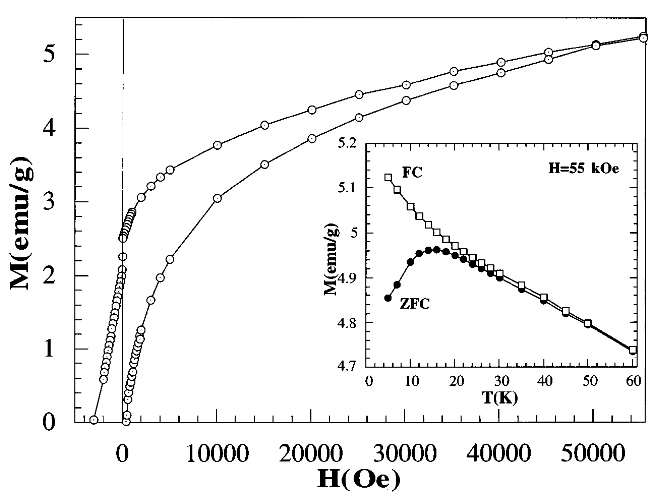

FIG. 2. Detail of the $M(H)$ curve and the ZFC-FC process (inset) showing the high field irreversibility and the offset from zero of the hysteresis loop. Notice the very small value of M_S.

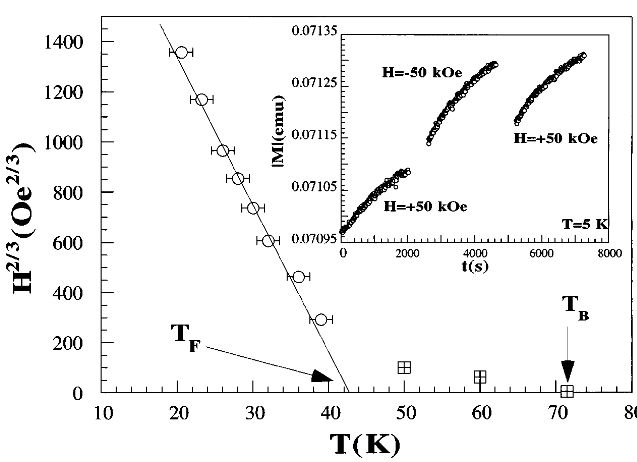

FIG. 3. Field dependence of the spin-glass transition temperature T_F showing the AT line, i.e., $\delta T_F \propto H^{2/3}$. T_F ($H = 0$) is obtained by extrapolating the AT line back to $H = 0$. Inset: Time dependence of the absolute value of the magnetization in applied fields of alternated sign after a ZFC process.

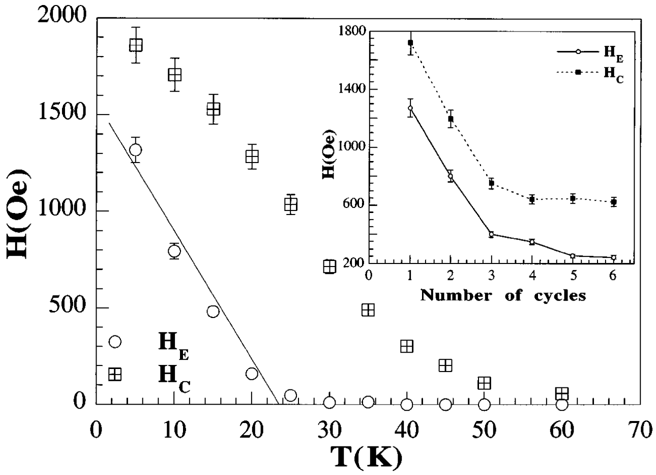

FIG. 4. Thermal behavior of the exchange anisotropy field H_E, and the coercive field H_C. The linear falloff $(1 - T/T_{\mathrm{crit}})$ of the former is observed according to the predictions of the random-field model of exchange anisotropy. Inset: Detail of the magnetic training effect in H_C and H_E.

a higher ordering temperature, is single domained. When the field is removed, the FM core experiences the field generated by the frozen surface layer in the direction of the previously applied field, generating the observed offset of the hysteresis loop. The temperature dependence of H_E is shown in Fig. 4. A linear falloff $(1 - T/T_{\mathrm{crit}})$ is observed according to the predictions of the random-field model of exchange anisotropy [19]. $T_{\mathrm{crit}} \approx 25$ K corresponds to the value at which $H_E \approx 0$ Oe and, as expected, it is below the spin-glass transition temperature $T_F \approx 42$ K, because H_E can only exist while the surface spin-glass layer is frozen with a preferred orientation generated with a FC process in high field.

In the framework of the above theory, developed for an AF/F sandwich [19], the value of the exchange anisotropy field is given by

$$H_E = 2(A_A K_A)^{1/2}/M_F t_F \,, \tag{2}$$

where K_A and A_A are the uniaxial anisotropy energy and the exchange stiffness of the AF and M_F and t_F are the magnetization and the thickness of the F. Identifying the F with the FM core of the particles and the AF with the spin-glass layer, the particle core thickness t_c can be estimated from Eq. (2). Our results show that $H_E \approx 1500$ Oe, from Ref. [20] $A_A \approx 5 \times 10^{-7}$ erg/cm, $K_A \approx 4 \times 10^5$ erg/cm^3 [18], and assuming that in the core $M_S \approx 80$ emu/g, a core thickness of $t_c \sim 1.1$ nm is obtained, which is a quite reasonable number. Since the particle size is about 9 nm and the aspect ratio is $D/t \approx 4$, the thickness of the surface spin-glass layer results about $(t - t_c)/2 \approx 0.6$ nm thick, in very good agreement with other estimates of the nonmagnetic layer in $MnFe_2O_4$ (0.7 nm [21]). On the other hand, Fig. 4 clearly shows that the strong increase in H_C occurs just below T_F signaling the close relation between H_C and the freezing of the surface spin glass. Therefore, the increase of the coercivity can be attributed to the extra energy required for the switching of the spins that are pinned by the exchange interactions with the frozen spin-glass surface layer.

In summary, we have made evident the existence of a low temperature surface spin-glass layer that becomes frozen below $T_F \approx 42$ K. The spin-glass nature is demonstrated by the field dependence of T_F following the well known AT line. Relaxation experiments and strong exchange anisotropy indicate the existence of a FM core surrounded by a spin-glass surface layer. An evaluation of the thickness of the spin-glass surface layer (≈0.6 nm) can be done by using the random-field model of exchange anisotropy, a model that also gives a proper description of the thermal dependence of H_E. The close relation between H_C and H_E demonstrates that the low temperature increase of H_C is due to the pinning effect of the frozen spin-glass surface layer upon the single-domained core.

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[1] *Magnetic Properties of Fine Particles*, edited by J. L. Dorman and D. Fiorani (North-Holland, Amsterdam, 1992).
[2] C. Kittel, Phys. Rev. **70**, 965 (1946).
[3] I. S. Jacobs and C. P. Bean, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press, New York, 1963), Vol. 3, Chap. 6.
[4] E. M. Chudnovsky and L. Gunther, Phys. Rev. Lett. **60**, 661 (1988).
[5] E. F. Kneller and F. E. Luborsky, J. Appl. Phys. **34**, 656 (1963).
[6] A. E. Berkowitz, W. J. Shuele, and P. J. Flanders, J. Appl. Phys. **39**, 1261 (1968).
[7] J. M. D. Coey, Phys. Rev. Lett. **27**, 1140 (1971).
[8] A. H. Morrish, K. Hanada, and P. J. Schurer, J. Phys. C **37**, 6 (1976).
[9] T. Okada, H. Sekizawa, F. Ambe, and T. Yamada, J. Magn. Magn. Mater. **31–34**, 105 (1983).
[10] F. T. Parker, M. W. Foster, D. T. Margulies, and A. E. Berkowitz, Phys. Rev. B **47**, 7885 (1993).
[11] S. Linderoth, P. V. Hendriksen, F. Bødker, S. Wells, K. Davis, S. W. Charles, and S. Mørup, J. Appl. Phys. **75**, 6583 (1994).
[12] D. Lin, A. C. Numes, C. F. Majkrzak, and A. E. Berkowitz, J. Magn. Magn. Mater. **145**, 343 (1995).
[13] A. H. Morrish and K. Haneda, J. Appl. Phys. **52**, 2496 (1981).
[14] R. H. Kodama, A. E. Berkowitz, E. J. McNiff, Jr., and S. Foner, Phys. Rev. Lett. **77**, 394 (1996).
[15] H. Maletta and W. Zinn, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1989), Vol. 12, Chap. 84; J. R. L. de Almeida and D. J. Thouless, J. Phys. A **11**, 983 (1978).

[16] A. Rouanet, H. Solmon, G. Pichelin, C. Roucau, F. Sibieude, and C. Monty, Nanostruct. Mater. **6**, 283 (1995).
[17] C. Roucau (unpublished).
[18] B. Martínez, A. Roig, X. Obradors, E. Molins, A. Rouanet, and C. Monty, J. Appl. Phys. **79**, 2580 (1996).
[19] A. P. Malozemoff, Phys. Rev. B **35**, 3679 (1987); J. Appl. Phys. **63**, 3874 (1988).
[20] Kezhao Zhang and D. R. Fredkin, J. Appl. Phys. **79**, 5762 (1996).
[21] Z. X. Tang, C, M. Sorensen, K. J. Klabunde, and G. C. Hadjipanayis, Phys. Rev. Lett. **67**, 3602 (1991).