Disordered Magnetism at the Grain Boundary of Pure Nanocrystalline Iron

E. Bonetti,[1] L. Del Bianco,[1,*] D. Fiorani,[2] D. Rinaldi,[3] R. Caciuffo,[3] and A. Hernando[4]
[1]*Istituto Nazionale per la Fisica della Materia and Dipartimento di Fisica, Università di Bologna, I-40127 Bologna, Italy*
[2]*Istituto di Chimica dei Materiali-CNR, C.P. 10, 00016 Monterotondo Stazione (Roma), Italy*
[3]*Istituto Nazionale per la Fisica della Materia and Dipartimento di Scienze dei Materiali e della Terra, Università di Ancona, I-60131 Ancona, Italy*
[4]*Instituto de Magnetismo Aplicado UCM-Renfe, P.O. Box 155, E-28230 Las Rozas, Madrid, Spain*
(Received 1 July 1999)

The low-temperature magnetic behavior of ball-milled nanocrystalline Fe is reported. The results of dc and ac susceptibility, remanence, and magnetic relaxation measurements indicate a transition from a high-temperature ferromagnetic state to a low-temperature disordered regime, where a collective freezing of the crystallites magnetic moments occurs. It is proposed that the behavior is determined by the presence of the structurally disordered grain boundaries, showing spin-glass-like properties.

PACS numbers: 75.50.Kj, 75.50.Bb, 75.50.Lk

The macroscopic behavior of nanostructured magnetic systems is determined by the structure, size, and morphology of the constituent phases and by the type and strength of magnetic coupling between them. For an assembly of noninteracting particles, the magnetic properties depend mainly on their volume: For instance, single-domain particles can show superparamagnetic behavior when their thermal energy becomes comparable to the anisotropy energy barrier for moment reversal, a quantity which is proportional to the particle volume [1]. Interparticle interactions (dipole-dipole or exchange interactions) compete with the anisotropy energy in determining the orientation of the particle moments. If strong enough, these interactions may turn the collection of individual superparamagnetic relaxation processes into a collective dynamical behavior [2]. Similarly, intercrystallite interactions dominate the magnetic properties of bulk nanocrystalline materials, characterized by the presence of grains with nanometric dimensions and a significant fraction of grain boundaries (or interfaces). In this case, however, the interactions are transmitted through the interfaces, and the magnetic behavior is determined by the structural features and the related magnetic character of the grain boundaries.

Within this context, in this Letter we describe the low-temperature magnetic behavior of ball-milled nanocrystalline iron, investigated by performing magnetization, dc, and ac susceptibility measurements. The results clearly indicate that a frequency-dependent transition takes place at temperature lower than about 70 K, which is interpreted as a passage from a high-temperature ferromagnetic state to a low-temperature disordered state, similar to a spin-cluster glass. To our best knowledge, it is the first time that such a behavior has been observed in pure nanocrystalline iron and it is proposed that it originates from the tendency of the disordered interfaces to show spin-glass-like properties.

Nanocrystalline Fe was prepared by a mechanical energy transfer technique, through ball milling. Pure iron precursor powders (99.9% purity, 325 mesh) were milled for 120 h in an originally assembled planetary mill [3] operating in a vacuum of 10^{-6} mbar and $T = 220$ K, using hardened steel vials and balls. The ball to powders weight ratio was 10:1. The as-milled powders were analyzed by x-ray diffraction: An average grain size of (12 ± 2) nm and a microstrain of the order of 4×10^{-3} were estimated according to the Warren-Averbach method [4]. Energy dispersive x-ray analysis has been carried out to check the presence of impurities. The results obtained are in line with previous determinations [5] and allow us to exclude the presence of impurities deriving from the milling tools, at least in an amount greater than 0.1 at. %.

In Fig. 1, we show the temperature dependence of zero-field-cooled (M_{ZFC}) and field-cooled (M_{FC}) magnetization, as measured by a Quantum Design SQUID magnetometer for increasing values of the temperature T (applied field $H = 50$ Oe). While M_{FC} is constant in the whole investigated temperature range (5–300 K), below

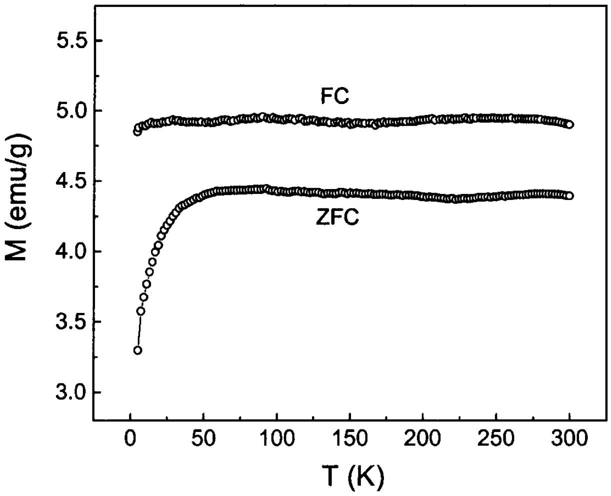

FIG. 1. Magnetization as a function of temperature, measured after zero-field cooling (ZFC) and field cooling (FC). Applied magnetic field $H = 50$ Oe.

about $T = 70$ K, M_{ZFC} decreases more and more rapidly with decreasing temperature.

The real (in-phase) and imaginary (out-of-phase) components of the ac magnetic susceptibility were measured as a function of temperature with a LakeShore 7000 system using the mutual-inductance technique. Data were collected on warming from 13 to 300 K after zero-field cooling of the sample. The calibration was performed with a $Gd_2(SO_4)_3 \cdot 8H_2O$ paramagnetic standard having the same shape and size as the investigated samples. Figure 2 shows the results obtained with a driving field of amplitude $H_0 = 100$ A/m, oscillating at different frequencies in the 1–10 kHz range. With decreasing temperature below about $T = 70$ K, the in-phase susceptibility component χ' is seen to depend strongly on frequency, which reflects a marked slowing down of the dynamics [Fig. 2(a)]. Moreover, χ' shows a rapid decrease below a frequency-dependent temperature [Fig. 2(a)] which is accompanied by a well-defined peak in the imaginary component χ'' [Fig. 2(b)], confirming the presence of relaxation processes.

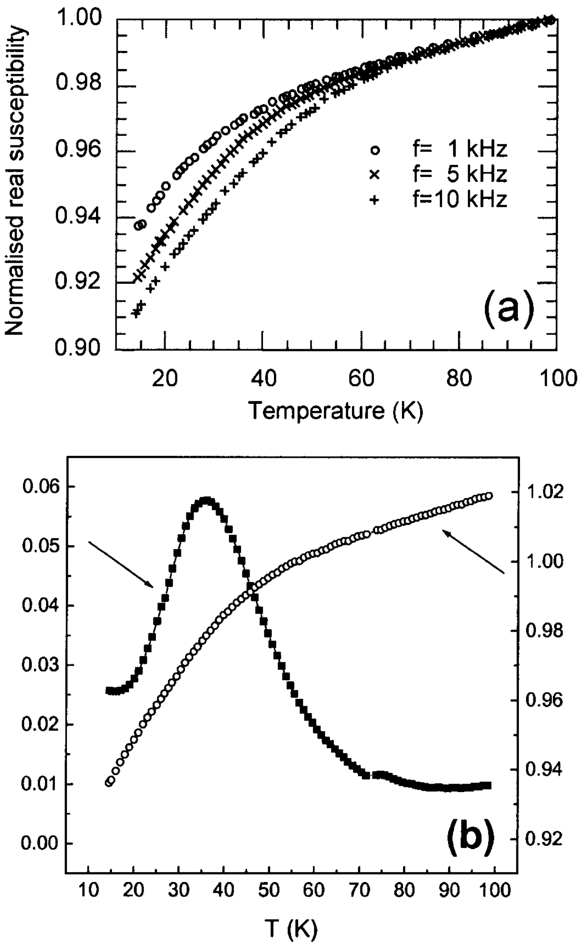

FIG. 2. (a) Real part of the ac susceptibility as a function of temperature, measured for three different frequencies (1, 5, and 10 kHz) of the driving field (field amplitude $H_0 = 100$ A/m). The data are normalized to the value recorded at $T = 100$ K. (b) Real and imaginary components of the ac susceptibility as a function of temperature at the frequency of 7500 Hz.

The behaviors, described above, recall the features of a reentrant spin glass [6] and suggest a transition from a high-temperature ferromagnetic state to a low-temperature disordered frozen magnetic state. The high-temperature, ferromagnetic regime is also confirmed by Mössbauer spectroscopy measurements which do not reveal the presence of a paramagnetic component in the range from 77 to 300 K, in general agreement with previous investigations [7].

To gain more information on the dynamical magnetic behavior, magnetization relaxation measurements were performed at different measuring temperatures ($T_m = 20$, 30, 70, and 250 K) by a SQUID magnetometer. The measurements were performed as follows: First the sample was cooled in zero field down to T_m; at T_m, 10 s elapsed (waiting time, t_w) before the application of the magnetic field ($H = 50$ Oe), and then the time variation of M_{ZFC} was recorded. At the end of this first measurement, the field was removed and the temperature was raised to 300 K, lowered again at the same T_m than before, and, after $t_w = 1000$ s, the magnetic field was applied and the time variation of M_{ZFC} recorded again. In Fig. 3, time-relaxation measurements of M_{ZFC} at $T_m = 20$ and 70 K are shown. The magnetization relaxes with time and, at 20 K, is clearly dependent on the waiting time, i.e., the M_{ZFC} value is lower in the measurement carried out after waiting for 1000 s [Fig. 3(a)]. The waiting-time effect is reduced at $T_m = 30$ K and disappears at $T_m = 70$ K [Fig. 3(b)]. The waiting-time dependence supports the existence of a collective frozen magnetic state at low temperature. Indeed, the aging effect is usually observed in disordered spin systems governed by a correlated dynamics and it is consequence of the onset, with decreasing temperature, of a very complex multivalleys phase space, with many quasidegenerate energy minima [8]. It is also noteworthy that the M_{ZFC} was found to relax with time in the whole investigated temperature range: The explanation is proposed below.

The origin of the described behavior is found in the nanocrystalline structure of the analyzed sample. It must be considered that ball milling is a nonequilibrium processing tool, particularly suitable for the synthesis of various metastable structures: amorphous materials, extended solid solutions, and the solid solution of immiscible elements [9]. Peculiar to this technique, in comparison with high-equilibrium synthesis methods, is the possibility to prepare nanocrystalline metallic phases presenting metastability on different levels. In fact, the mean grain size is not the only parameter characterizing the structure and hence the physical behavior of pure nanostructured metals. The thermodynamic state of the interfaces, which can be controlled by a tailoring of the synthesis parameter [10–12], is also found to affect many physical properties [3,13]. According to a wide number of research works

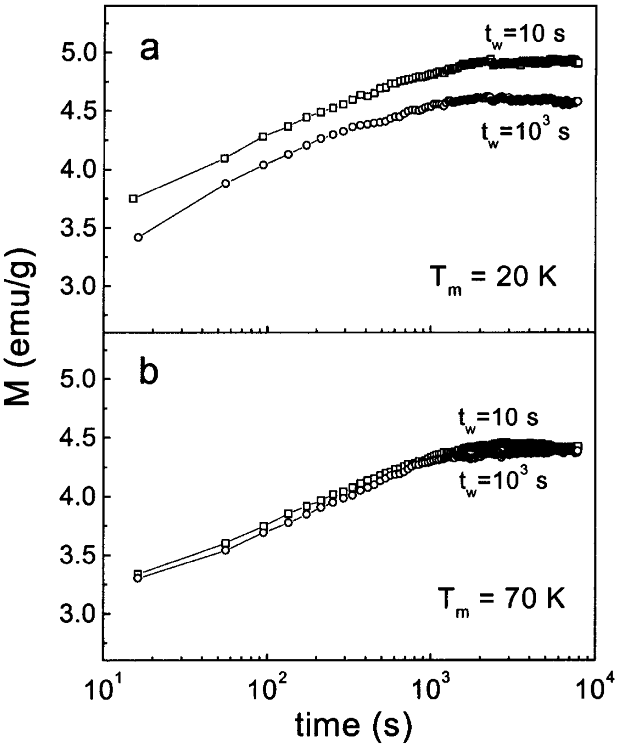

FIG. 3. Time dependence of the zero-field-cooled magnetization, measured at $T_m = 20$ K (a) and $T_m = 70$ K (b) for two different waiting times (10 and 1000 s).

on far-from-equilibrium nanocrystalline metals, the interfaces present a reduced atomic coordination compared to the crystals [10,12] and, therefore, the atomic arrangement at the grain boundary may be considered close to the amorphous configuration [14]. Indeed, in some cases, nanocrystalline materials have been found to exhibit a two-phase character due to the presence of the crystalline and of the grain boundary region [7,15]. In high-energy ball-milled Fe, the thermally induced rearrangement of the grain boundaries was found to result in the formation of a magnetically ordered fcc phase, stable at room temperature [16]: This constitutes a good example of the peculiarity of the interfaces atomic configuration in nanocrystalline materials compared to the stable, coarse-grained counterparts.

In regards to pure Fe, the structural disorder and the wide distribution of interatomic spacings at the interfaces [7] are expected to result in a distribution of anisotropy directions and a distribution, in magnitude and even in sign, of exchange interactions. In analogy to what has been proposed for surface spins of small ferrimagnetic particles [17] or for boundary spins in antiferromagnetic ball-milled Fe-Rh [18], the combination of topological disorder and competing magnetic interactions can lead to a spin-glass-like character of the interface region. Indeed, it is worth noting that amorphous Fe is not accessible to experiments, but extrapolations of the magnetic behavior of amorphous Fe-Zr alloys to pure amorphous Fe [19] as well as *ab initio* band-structure calculations [20] predict for amorphous iron a spin glass or a speromagnetic behavior.

On account of the previous considerations, the experimental results reported here may be well interpreted in the following terms. At sufficiently high temperature, the magnetic domains extend over many grains since the crystallites are ferromagnetically coupled by exchange interaction, which dominates on the single crystallite anisotropy energy, leading to an averaging out of the effective anisotropy (indeed, the coercive field at room temperature is very low, $H_c \sim 3$ Oe). According to the random anisotropy model (RAM) for a two-phase system [21], this is expected to occur when the crystallites dimension is smaller than the ferromagnetic exchange length of the grain (L_g, which is around 20 nm for iron [22]), and the grain boundary thickness (δ) is smaller than the ferromagnetic exchange length of the interface (L_i). At any temperature, L_i may be supposed up to 1 order magnitude shorter than L_g. In fact, it is assumed that, due to the topological fluctuations in interatomic distances, the effective exchange stiffness parameter is smaller at the boundary than at the crystal's core, whereas the anisotropy may be enhanced, because of the lack of symmetry. Substantially, the condition $L_i > \delta$ implies that the spins at the grain boundary are oriented in the direction imposed by the surrounding environment: It is as if the boundary spins were polarized by the core of the ferromagnetic grains. However, the existence of irreversibility (difference between M_{FC} and M_{ZFC} curves in Fig. 1) and of relaxation phenomena even at 250 K indicates that the material is not an homogeneous ferromagnet. There should be some small crystallites which, maybe because of a less effective exchange coupling through the interface, do not join any of the large multigrain magnetic domains and behave as blocked superparamagnetic particles.

With reducing temperature, the anisotropy at the grain boundary grows large, and the links holding the boundary spins aligned to the magnetization vectors of the surrounding crystallites are progressively severed. Competing magnetic interactions stabilize a spin-glass-like state at the grain boundary. Since the boundary spins are frozen in random directions, the exchange interaction cannot be transmitted across the interfaces. In the context of the RAM, this is expressed saying that, with reducing temperature, the local anisotropy at the interface increases more rapidly than the exchange stiffness parameter [23] and increases so much that L_i becomes smaller than δ. Therefore the crystallites result uncoupled, but they are expected to strongly interact through dipole-dipole interactions, which can be ferromagnetic as well as antiferromagnetic. The consequent mixing of interactions, which competes with the magnetocrystalline anisotropy, is responsible for the random freezing of the grain moments.

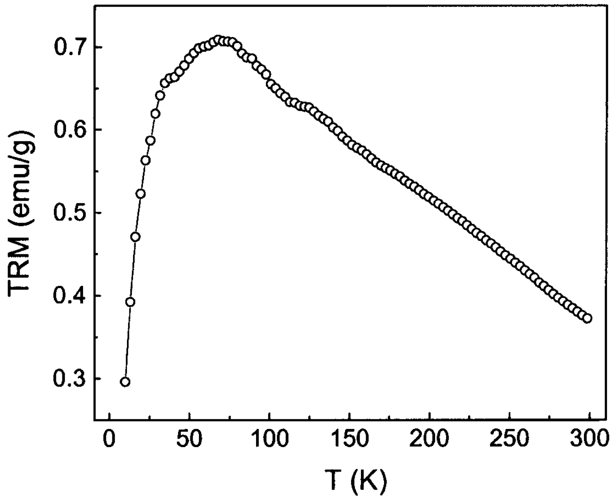

FIG. 4. TRM as a function of temperature.

Therefore, the freezing of the boundary spins implies that the whole system acts as a spin-cluster glass, which is fully coherent with the experimental results.

This explanation is also supported by the temperature dependence of the thermoremanent magnetization (TRM) (Fig. 4). The measurement was performed, by SQUID, as follows: First the sample was cooled down from $T = 300$ to 5 K in a field of 25 kOe; at 5 K, the field was removed and the remanence was measured for increasing values of temperature, up to 300 K. It is observed that, with decreasing temperature, TRM first increases, as expected for an assembly of ferromagnetic domains, but below 75 K, rapidly decreases. This is fully consistent with the onset and development of a collective frozen magnetic state with grain moments randomly oriented.

It must be pointed out that the magnetization measured at $T = 5$ K for an applied magnetic field of 50 kOe was about 220 emu/g, namely, very close to the saturation magnetization of bulk polycrystalline iron. This means that such magnetic field is sufficiently strong to fully align the randomly locked spins and, moreover, provides a further evidence of the excellent purity of the analyzed samples.

It is worth remarking that the only hypothesis of an evolution of L_i with temperature, following a change in the exchange stiffness to anisotropy ratio, could not account for the experienced frequency dependence of the susceptibility if a slowing down of the spins dynamics was not also invoked. The spin-glass-like freezing of the grain boundary region should be the main responsible for the change in the interaction regime, from a ferromagnetic regime, exchange interactions controlled, to a cluster spin-glass-like regime, where the random freezing of the grain moments is determined by both magnetocrystalline anisotropy and dipole-dipole interactions.

Finally, it should be pointed out that experimental results compatible with spin-glass-like properties have been recently obtained for different nanostructured compounds produced by ball milling [18,24]. In light of our results, it seems possible to conclude that the collective-dynamics behavior is inherent to the nanocrystalline character of these magnetic systems and not strictly dependent on their chemical composition.

This work has been supported by the Istituto Nazionale per la Fisica della Materia (INFM)-Sezione D, under Project No. PASS-97.

---

*Corresponding author.
Present address: Dipartimento di Fisica, Università di Bologna, Viale Berti Pichat 6/2, 40127 Bologna, Italy.
Email address: delbianco@df.unibo.it

[1] C. P. Bean and J. D. Livingston, J. Appl. Phys. **30**, 120S (1959); J. L. Dormann, D. Fiorani, and E. Tronc, Adv. Chem. Phys. **98**, 283 (1997).
[2] J. L. Dormann *et al.*, Phys. Rev. B **53**, 14 291 (1996); H. Mamiya, I. Nakatani, and T. Furubayashi, Phys. Rev. Lett. **80**, 177 (1998); T. Jonsson, P. Svedlindh, and M. F. Hansen, Phys. Rev. Lett. **81**, 3976 (1998).
[3] E. Bonetti *et al.*, J. Appl. Phys. **84**, 4219 (1998).
[4] B. E. Warren, *X-Ray Diffraction* (Dover Press, Cambridge, 1990).
[5] L. Del Bianco *et al.*, Phys. Rev. B **59**, 14 788 (1999).
[6] B. R. Coles, B. V. B. Sarkissian, and R. H. Taylor, Philos. Mag. B **37**, 489 (1978).
[7] L. Del Bianco *et al.*, Phys. Rev. B **56**, 8894 (1997).
[8] T. Jonsson *et al.*, Phys. Rev. Lett. **75**, 4138 (1995).
[9] C. C. Koch, Nanostruct. Mater. **2**, 109 (1993).
[10] J. Löffler and J. Weissmüller, Phys. Rev. B **52**, 7076 (1995).
[11] K. Reimann and R. Würshum, J. Appl. Phys. **81**, 7186 (1997).
[12] A. Di Cicco *et al.*, Phys. Rev. B **50**, 12 386 (1994).
[13] E. Bonetti *et al.*, Nanostruct. Mater. **10**, 741 (1998).
[14] K. Lu and N. X. Sun, Philos. Mag. Lett. **75**, 389 (1997).
[15] S. Trapp *et al.*, Phys. Rev. Lett. **75**, 3760 (1995).
[16] L. Del Bianco *et al.*, Phys. Rev. Lett. **81**, 4500 (1998).
[17] R. H. Kodama *et al.*, Phys. Rev. Lett. **77**, 394 (1996).
[18] A. Hernando *et al.*, Phys. Rev. B **58**, 5181 (1998).
[19] D. H. Ryan *et al.*, Phys. Rev. B **35**, 8630 (1987).
[20] M. Liebs and M. Fähnle, Phys. Rev. B **53**, 14 012 (1996).
[21] J. Arcas *et al.*, Phys. Rev. B **58**, 5193 (1998).
[22] H. Kronmüller, Nanostruct. Mater. **6**, 157 (1995).
[23] A. Hernando *et al.*, Phys. Rev. B **58**, 366 (1998).
[24] G. F. Zhou and H. Bakker, Phys. Rev. Lett. **72**, 2290 (1994); **73**, 344 (1994); I. W. Modder and H. Bakker, Phys. Rev. B **58**, 14 479 (1998).