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Hysteresis shift in Fe-filled carbon nanotubes due to γ-Fe

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The phase distribution of high aspect ratio, Fe-filled carbon nanotubes prepared by pyrolyzing a mixture of powered ferrocene and C_{60} has been determined by means of Mössbauer spectroscopy. Our results for that characterization are closely related to the observation, after field cooling processes, of a hysteresis loop shift and clearly suggest a spatial phase distribution which includes the presence of a γ-Fe/α-Fe interface. The temperature dependence of the hysteresis loop shift is discussed in terms of localized regions at that interface exhibiting uncompensated antiferromagnetism within reduced dimensions.

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Since their first synthesis carbon nanotubes have been appreciated by their unique combination of electronic and mechanical properties[1,2] that make them a very promising candidate system to be used on the development of a broad range of new devices, which already includes field emission lamps, nanotransistors, spin polarized electron sources, flat display panels, and hydrogen storing systems.[3,4] Nevertheless, one of the most natural and attractive possibilities of these materials, closely linked to their morphology and extremely high aspect ratio, is their use as nanocontainers for secondary phases and, particularly, for magnetically ordered ones.[5] In fact, the encapsulation of magnetic phases in carbon nanotubes could constitute, due to the very large magnetic shape anisotropies acting on the encapsulated material, a feasible approach to, on the one side, the achievement of magnetic order stabilization against thermal fluctuations in systems having extremely reduced dimensions and, on the other, the exploration of the physics of the magnetic order in close-to-one-dimensional structures. From the point of view of the practical uses, carbon nanotubes filled with magnetic phases could also develop giant coercivities (coercivity values above those predictable on the basis of the bulk magnetocrystalline anisotropy) linked to their reduced transverse dimension and the consequential large influence on the magnetization reversal phenomenology of the reduced symmetry, high anisotropy interfaces. The control of the coercivity of these magnetic phase-filled nanotubes would make possible their use as very high density recording media, as magnetoresistive elements suitable to be packed to high densities, as probes for magnetic force microscopy, and, even, as recording heads.

In this work, we present and discuss results about the structural and magnetic properties of Fe-filled nanotubes. We will show how the presence in the as-prepared samples of antiferromagnetic fcc γ-Fe results, through the coupling to bcc α-Fe, on the occurrence of the so-called exchange biasing a phenomenology underlying the operation of the spin valves, one of the most relevant developments of the magnetoelectronics.

Fe-filled carbon nanotubes were prepared by pyrolyzing a 1:1 mixture (by weight) of powered ferrocene and C_{60} at atmospheric pressure under an Ar atmosphere at 1050 °C. This procedure[6] generates carpetlike flakes or films (2 mm^2; <40 μm thick) of aligned Fe-filled carbon nanotubes. The encapsulated nanowires, exhibited single crystalline-type electron diffraction patterns,[6] and dimensions ranging from 5 to 40 nm outer diameter (OD) and <10 μm in length. The carbon tubes, which coat the wires, have external diameters of 20–70 nm OD, and <40 μm in length.[6] ^{57}Fe Mössbauer data were recorded in the transmission mode with a conventional constant acceleration spectrometer and a ^{57}Co (Rh) source. Low temperature spectra were recorded between 298 and 18 K using a He-closed cycle criogenerator. All the isomer shifts were referred to the centroid of the α-Fe sextet at room temperature. Low temperature magnetic characterization was carried out in the range from 5 up to 300 K by using a SQUID magnetometer under applied fields <5 T. The evolution of the magnetization and the coercive force were measured after zero field (ZFC) and field cooling (FC) processes. The high temperature properties (300–1000 K) were measured by using a vibrating sample magnetometer under a maximum field of 0.15 T.

All the Transmission Mössbauer spectra (Fig. 1) contained three different components: two sextets and a singlet. The Mössbauer parameters obtained from the fit of the room temperature spectra for the most intense sextet ($\delta = 0.00\ \mathrm{mm\,s^{-1}}, \Delta = 0.00\ \mathrm{mm\,s^{-1}}, H = 33.0\ \mathrm{T}$, area $= 50\%$), corresponded unequivocally to α-Fe. The room temperature Mössbauer parameters of the second sextet ($\delta = 0.23\ \mathrm{mm\,s^{-1}}, \Delta = 0.10\ \mathrm{mm\,s^{-1}}, H = 20.2\ \mathrm{T}$, area $= 20\%$) are characteristic of Fe_3C.[7] High temperature magnetization measurements showed two magnetic transitions: the first one, at around 530 K, was attributed to the order transition of the Fe_3C phase. The second one, at around 1000 K, was identified with the Curie point of α-Fe. The room temperature isomer shift of the singlet ($\delta = -0.11\ \mathrm{mm\,s^{-1}}$, area $= 30\%$) is similar to that shown by γ-Fe.[7] As the temperature decreases from 298 K down to around 100 K, and as it could

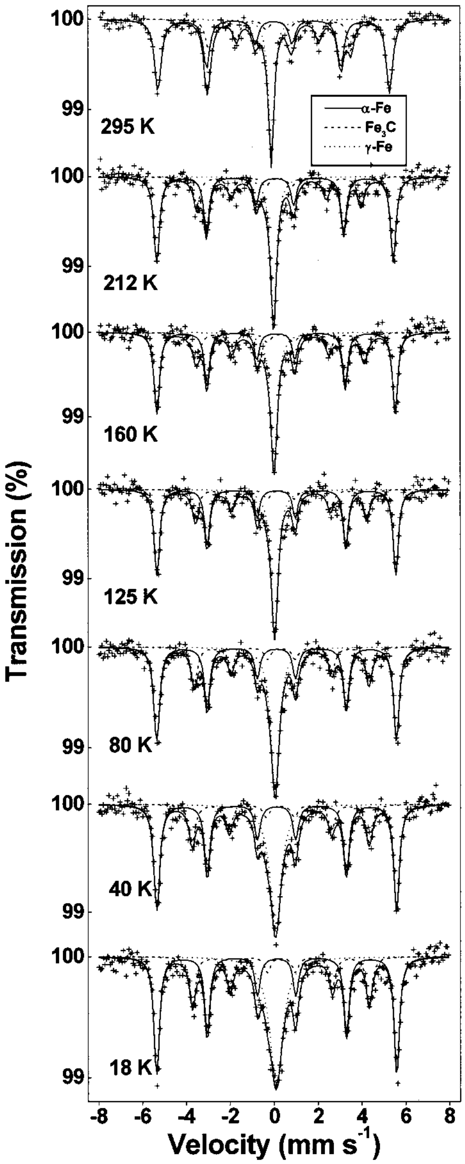

FIG. 1. ^{57}Fe transmission Mössbauer spectra recorded between 18 and 295 K from the iron-containing nanotubes sample.

be expected, both the hyperfine magnetic fields of the α-Fe and Fe$_3$C components and the linewidth of the singlet Γ_{sin} increase (see Fig. 2). At around 100 K, Γ_{sin} suffers an abrupt change of increase rate. Both the shape of this Γ_{sin} vs T curve and the linewidth values measured at low temperatures resemble those reported for γ-Fe (Ref. 8) and therefore confirm the assignment of the singlet to that Fe phase (the kink at around 90–100 K in Fig. 2 should correspond to the onset of antiferromagnetic order of fcc, γ-Fe). The relative spectral areas of the different components remain about the same at any given temperature. This precludes the possibility of the existence of a superparamagnetic α-Fe fraction contributing to the observed singlet at room temperature. The existence of contributions corresponding to iron oxides is also discarded. Similar spectra, containing α-Fe, Fe$_3$C, and γ-Fe contributions, have been reported in studies about the magnetic properties of iron in nanocapsules.[9] In this context, x-ray powder diffraction studies (results not shown) confirm the presence of small γ-Fe domains.

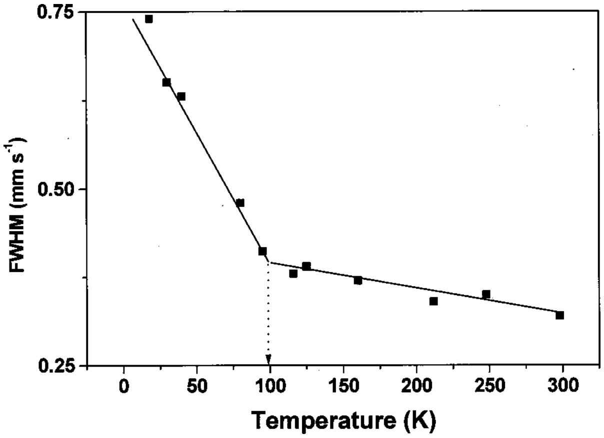

FIG. 2. Variation with temperature of the linewidth of the singlet.

The thermal evolution of the magnetization measured, after ZFC and FC processes, under an applied field of 5 T is shown in Fig. 3. The ZFC and Fc curves coincide up to around 50 K and they split below that temperature. A similar behavior has been reported to occur in ZFC-FC high field processes measured in Fe nanoparticles coated with a Fe$_2$O$_3$ shell. In that case, the antiferromagnetic character of the Fe$_2$O$_3$ was in the origin of the low temperature irreversibility.[10] Thus, we attribute our results to the combination of ferromagnetic-antiferromagnetic (α-Fe/γ-Fe) exchange and high antiferromagnetic (γ-Fe) anisotropy which is known as exchange induced anisotropy.[11] Consequently, both phases should have a common interface and, from this, we will consider that the samples are formed by an inner α-Fe core surrounded, from inside to outside, by γ-Fe, Fe$_3$C, and carbon layers. The increase with the temperature of the ferromagnetic phase magnetization is correlated to the fact that at the lowest temperature and after a ZFC process, the α-Fe moments are not fully aligned with the large applied field. The observation of an increase of the ZFC magnetization corresponding to a 4% of the minimum temperature FC

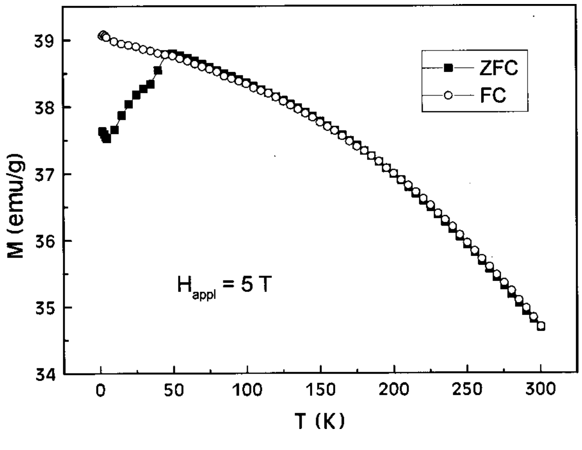

FIG. 3. Thermal dependence of the 5 T magnetization measured after ZFC and FC processes.

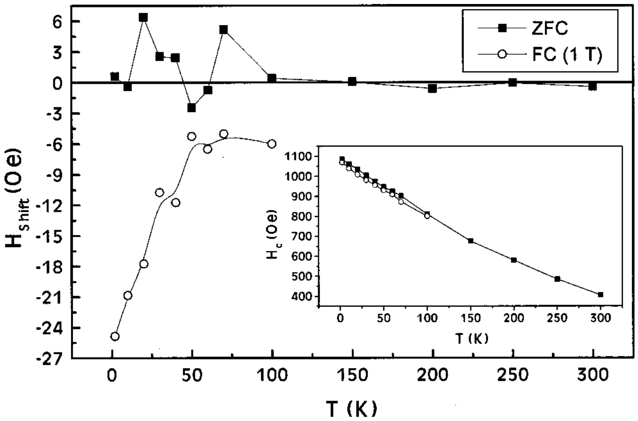

FIG. 4. Thermal dependence of the hysteresis loop shift measured, after ZFC and FC (1 T) processes, under a maximum applied field of 5 T. The inset shows the temperature dependence of the 5 T, ZFC, and FC coercivities.

magnetization value clearly means that the α-Fe/γ-Fe coupling results in a α-Fe hardening that a 5 T applied field is not able to overcome. It is known[11] that in the systems exhibiting exchange induced anisotropy, which are cooled from above the Néel temperature of the antiferromagnetic phase under the action of an applied field, the local coupling is polarized and the observed macroscopic effect associated to that polarization corresponds to a shift of the hysteresis loop in the sense of the fields opposite to that applied during the cooling process. That effect is also observed in our Fe-filled carbon nanotubes. Figure 4 displays the temperature dependence of the hysteresis loops shift, measured under a maximum applied field of 5 T after ZFC and FC (1 T) the samples. Our results evidence that the measured shift is negligible in the case of the ZFC samples and also that the FC shift markedly increases with the decrease of the temperature below around 100 K. We should point out in that respect that the α-Fe$-$$\gamma$-Fe coupling does not evolve with the temperature as it could be expected if it were associated to the onset of the antiferromagnetic order in a bulklike Néel transition. In that case, the only expected variation with the temperature of the loop shift, below the order temperature of the antiferromagnet, should be linked to the temperature dependence of the antiferromagnetic anisotropy which typically is proportional to $M_S^n(T)$ (with $n=2-3$) and therefore corresponds to a much weaker temperature evolution[12] than that observed for the loop shift variation rate. The broad range of temperatures in which the loop shift increases with temperature could be understood on the basis of the occurrence at the ferromagnetic-antiferromagnetic interface of a distribution of local properties. More concretely, and taking into account the fact that the coupling develops at temperatures below the Néel temperature of the γ-Fe, the observed rapid increase of the loop shift magnitude with the decrease of the temperature is compatible with the presence of reduced sized antiferromagnetically uncompensated centers, which due to the thermal fluctuations only get ordered at temperatures below the bulk Néel temperature. In this simple picture, clearly similar to the conventional description of the superparamagnetic phenomenology, the distribution of local ordering (blocking) temperatures should directly reflect that of local anisotropies. The inset in Fig. 4 shows the thermal evolution of the saturation (5 T) coercivity after ZFC and FC processes. It is noteworthy that the high coercivity obtained is not compatible with the bulk α-Fe anisotropy constants.[13] This feature should be attributed to the combination of three effects: first, to the reduced transverse dimensions of the nanotubes, which are of the order or lower than the α-Fe exchange correlation length,[14] second, to the high magnetic anisotropy of the fcc/bcc interface (related to its reduced symmetry) and finally, and below 100 K, to the hardening linked to the occurrence of coupling at the γ-Fe/α-Fe interface. According to the experimental magnitudes of the loop shift, the FC coercivity and that of the difference between the FC and ZFC coercivities, the influence on the reversal field of the interfacial anisotropy should be larger than that of the exchange induced anisotropy. This result is in evident correspondence with the single crystalline character of the Fe phases.

In summary, from the Mössbauer and hysteretic characterization, we propose that the occurrence in our nanotubes of a phase distribution consisting of a α-Fe core surrounded by γ-Fe, Fe_3C, and carbon layers. The occurrence of exchange induced anisotropy at the ferromagnetic, α-Fe-antiferromagnetic, γ-Fe interface determines both the thermomagnetic and the hysteretic behaviors. Concretely, the occurrence of interfacial, antiferromagnetically uncompensated local neighborhoods is in the origin of the high field irreversibility observed in the ZFC and FC curves and also in that of the hysteresis loop shift and its temperature dependence. Differently from this, we propose the magnitude of the saturation coercive force seems to be primarily linked to the reduced symmetry of the fcc/bcc interface.

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