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Magnetic transitions in α-Fe_2O_3 nanowires

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Magnetic transitions in single-crystal α-Fe_2O_3 (hematite) nanowires, grown by thermal oxidation of iron powder, have been studied in the range of 5–1023 K with a superconducting quantum interference device below room temperature and with a vibrating sample magnetometer at higher temperatures. The broad temperature range covered enables us to compare magnetic transitions in the nanowires with the transitions reported for bulk hematite. Morin temperatures (T_M) of the nanowires and of hematite bulk reference powder were found to be 123 and 263 K, respectively. Also the Néel temperature (T_N) of the nanowires, 852 K, was lower than the bulk T_N value. Measurements of the magnetization as a function of temperature show an enhanced signal in the nanowires, which suggests a decrease in the antiferromagnetic coupling. A coercive field observed below T_M in the hysteresis loops of the nanowires is tentatively explained by the presence of a magnetic phase. © *2009 American Institute of Physics*. [doi:10.1063/1.3259394]

I. INTRODUCTION

Physical properties of nanostructures attract increasing interest for a wide range of theoretical studies and nanotechnology applications. In particular, α-Fe_2O_3 (hematite) is a stable material, with magnetic and semiconducting properties, which has applications as photocatalyst,[1] gas sensor,[2] field emitter,[3] field effect transistors,[4] drug delivery,[5] and others. Bulk α-Fe_2O_3 presents a magnetic transition at Morin temperature T_M of about 260 K. Below T_M, two magnetic sublattices are oriented along the rhombohedral (111) axis (*c*-axis) and are exactly antiparallel, inducing a uniaxial antiferromagnetic behavior. Above T_M, α-Fe_2O_3 displays weak ferromagnetism due to a small misalignment of the spins, created by a slight spin canting of the two magnetic sublattices. At the Néel temperature T_N of about 956 K, the common transition of antiferromagnetic materials takes place. However, the magnetic behavior has been found to be different in the case of nanosized material. For instance, T_M and T_N of polycrystalline hematite nanowires were reported[6,7] to be 80 and 350 K, respectively, much lower than those corresponding to the bulk material. The synthesis and characterization of hematite nanowires have been described in other works[8–13] and different values of the Morin temperature have been reported. In the present work, α-Fe_2O_3 nanowires have been grown by a thermal treatment of compressed Fe powder under argon flow. Morphological and structural characterizations of the nanowires were carried out by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and x-ray diffraction (XRD). The magnetic properties of these nanostructures, including T_N and T_M transition temperatures and hysteresis behavior, have been investigated with a superconducting quantum interference device (SQUID) or by vibrating sample magnetometry (VSM). The wide temperature range considered in our work, 5–1023 K, completely covers the transition temperatures reported for the bulk hematite.

II. EXPERIMENTAL METHOD

The experimental method used to grow the hematite nanowires has been previously described.[13] In brief, commercial Fe powder with 99.9% purity was ball milled in a centrifugal ball mill, and disk-shaped pellets, of about 7 mm in diameter and 2 mm thick, were prepared by compacting the powder under a compressive load. The pellets were then annealed at 700 °C for 10 h under argon flow. As the furnace was not sealed for high vacuum conditions, slow oxidation takes place during the thermal treatment, leading to the growth of hematite nanowires. The nanowires grow directly on the sample surface without the use of a catalyst or a foreign substrate. The structure and morphology of the wires were, in the first step, characterized by XRD and grazing incidence XRD using a Philips X'Pert PRO diffractometer and by SEM with a Leica 440 scanning electron microscope. HRTEM images were obtained using a field emission Jeol JEM 3000F microscope operating at 300 kV. For HRTEM characterization, the wires were released from the disks by sonicating the samples in butanol. Drops of the solution containing the nanostructures were then deposited onto carbon coated copper grids. For magnetic measurements, the wires were carefully detached from the pellets, avoiding any contact with metallic tools and introduced in the sample holders; a SQUID capsule or a boron nitride VSM holder. Prior to magnetic measurements, the VSM holders were ultrasonically cleaned and measured to check that no magnetic signal arose from them. The temperature dependence of the magnetization M(T) under an applied magnetic field of 1 kOe was measured in the 5–300 K range using a Quantum Design

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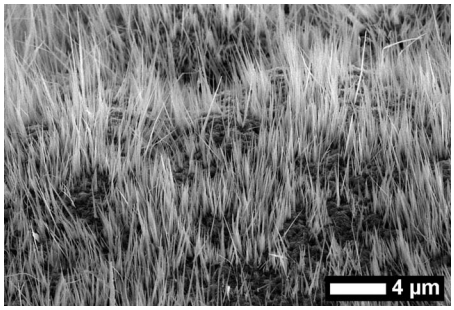

FIG. 1. SEM image of hematite nanowires grown at 700 °C (10 h).

SQUID. Hysteresis loops (M-H curves) were recorded up to applied field values of ±50 kOe. Further magnetic characterization in the temperature range of 300–1023 K was carried out with a Lakeshore 7304 VSM. In this case, the M(T) curves were recorded under an applied field of 5 kOe. Magnetic measurements were also carried out in commercial hematite powder (Sigma-Aldrich) for comparison purposes. The average grain size of this powder was 10 μm.

III. RESULTS AND DISCUSSION

After the thermal treatment at 700 °C, the disk appears covered by a dense array of nanowires, approximately perpendicular to the surface, with diameters of 100–200 nm and lengths of about 10 μm (Fig. 1). Most of the wires have uniform size along the length and terminate at a sharp tip. XRD patterns (not shown) reveal intense and sharp peaks that can be unambiguously indexed to rhombohedral α-Fe_2O_3 (a=5.038 Å, c=13.772 Å). HRTEM images and selected area electron diffraction (SAED) patterns of the nanowires (Fig. 2) show their single crystalline nature and that [110] direction is the usual growth direction of the wires. The HRTEM image of Fig. 2 shows the 0.251 nm fringe spacing in a nanowire, which corresponds to the (110) interplanar spacing of hematite. The thermal mechanism of the growth of the nanowires from the compacted Fe powder, in which diffusion processes seem to play a key role, has been discussed in Ref. 13.

Figure 3 shows the M(T) curves of α-Fe_2O_3 bulk reference powder and of the α-Fe_2O_3 nanowires. In the reference powder, a transition temperature of 262 K is observed, which

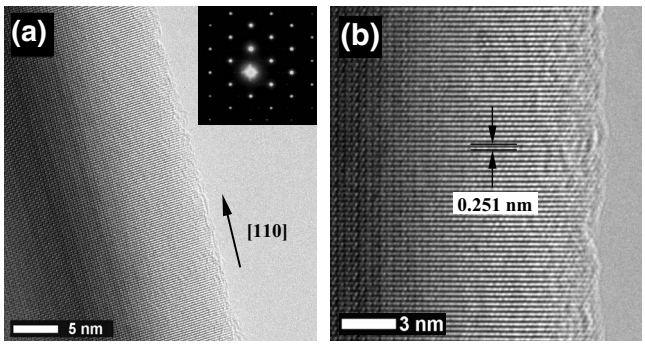

FIG. 2. (a) HRTEM image of a hematite nanowire. The corresponding SAED pattern, shown in the inset, corresponds to the (001) pattern of α-Fe_2O_3. (b) HRTEM micrograph of the same wire showing the (110) interplanar spacing of this material.

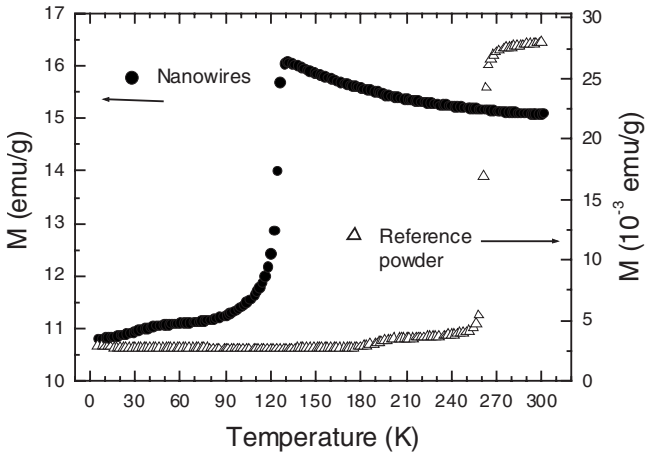

FIG. 3. Magnetization as a function of temperature for hematite nanowires and bulk reference powder in the 5–300 K temperature range.

corresponds to the reported Morin temperature (T_M) in bulk hematite, while the T_M value found for the nanowires is 123 K, as also shown in Fig. 3. T_M values lower than those of the bulk material have been reported for nanostructured α-Fe_2O_3. Zysler *et al.*[14] and Amin and Arajs[15] found a decrease in T_M, down to 186 K, with decreasing size of α-Fe_2O_3 nanoparticles, while a T_M of 216 K was reported[16] for dendritic α-Fe_2O_3 micropines. In the case of α-Fe_2O_3 nanowires, T_M values of 80 K (Ref. 7) and 125 K (Ref. 10) were reported. The low T_M of the nanowires of this work agrees with the behavior found in other nanostructures and is similar to that of Ref. 10. It has been suggested that the reduction in T_M in the hematite nanostructures may result from lattice strain and defects[16] or is due to uncompensated surface spins and/or shape effects of the nanowires.[10] Since these nanowires were removed from the surface of the pellets and introduced in the corresponding sample holder, any effect on the magnetic properties caused by the shape anisotropy will not be resolved in our experiments because the measurements are done on nanowires randomly oriented in the applied field. In the present case, XRD and HRTEM observations do not reveal the presence of high strains or extended defects in the nanowires. The Néel temperature T_N of nanowires or other nanosized structures of α-Fe_2O_3 has been much less investigated than their Morin temperature probably due to the difficulty of measuring small amounts of material at high temperature with reasonable signal to noise ratio. In this context, Yu *et al.* reported magnetic measurements up to the Néel temperature for the bulk material, with a transition temperature of about 600 K for α-Fe_2O_3 nanoparticle nanotube arrays grown by calcination of iron nanotubes.[17]

Figure 4(a) shows the M(T) curves, measured in the temperature range of 300–1023 K by VSM, of the reference hematite powder and the nanowires grown in this work. Both curves are represented together for comparison of the temperature dependence. Two important differences between both curves should be marked: first of all, the magnetic moment of the nanowires is much higher than that of the reference powder, as the respective y-axis scales show. Secondly, whereas the bulk sample shows a T_N value of about 960 K,

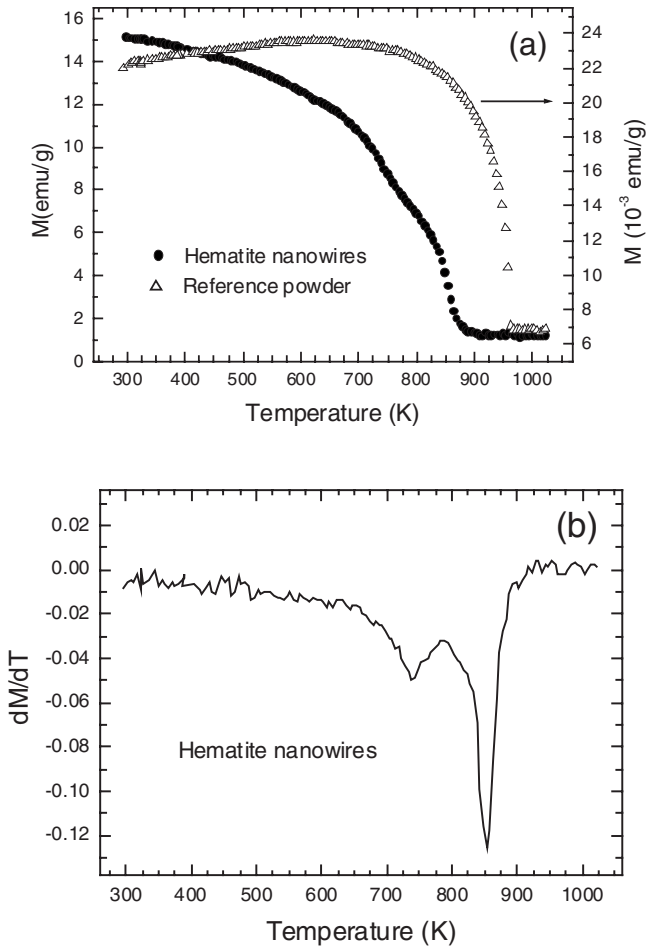

FIG. 4. (a) Magnetization as a function of temperature for α-Fe_2O_3 nanowires and bulk reference powder in the 300–1023 K temperature range. (b) dM/dT curve for hematite nanowires showing two transitions at 738 and 852 K (T_N).

close to the previously reported value, the T_N measured in the nanowires is 852 K. Therefore, both transition temperatures, T_M and T_N, have smaller values in our nanowires than in the bulk material. For T_N, the decrease of about 108 K found in our study is substantially smaller than the decrease previously reported for polycrystalline α-Fe_2O_3 wires.[7] In addition to the transition at Néel temperature of 960 K, a not very marked transition at 738 K is also observed in the M(T) curve of our hematite nanowires. This transition is clearly resolved in the derivative of the M(T) curve shown in Fig. 4(b).

The enhanced magnetic signal in the M(T) curve of the nanowires could be ascribed to the surface of these nanostructures, where the lack of symmetry could produce two different effects: on one hand, the antiferromagnetic coupling between atoms close to the surface of the nanowires may be smaller than in the core of the nanowire. This would lead to an easier alignment of magnetic moments under an applied field. On the other hand, the magnetic sublattices forming the antiferromagnetic structure may not be compensated in the surface area. In the latter case, the surface would behave as a ferrimagnetic material. Both effects, which cannot be distinguished in the M(T) curves, could explain the observed increase in the magnetization. The core of the nanowires,

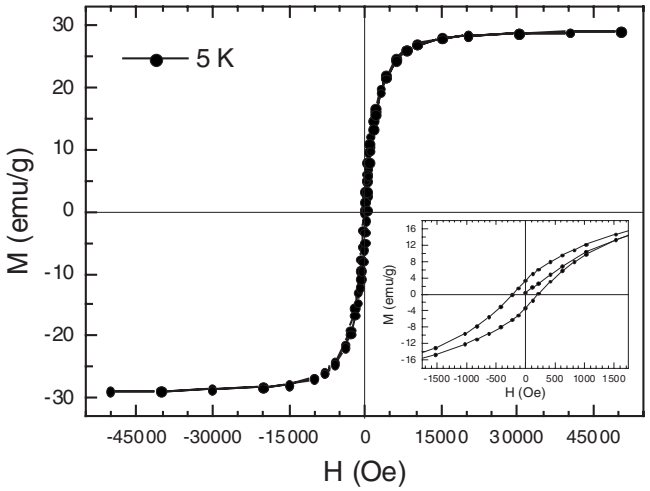

FIG. 5. Hysteresis loop for the hematite nanowires at 5 K. The inset shows the low applied field region in detail.

which is single crystalline, is expected to have a higher antiferromagnetic coupling, leading to a higher transition temperature, but smaller in any case than that characteristic of the bulk hematite.

Hysteresis loops measured at different temperatures show further differences between the magnetic properties of the nanowires and the reference powder and reinforce the hypothesis of two different regions in the nanowires as well. Figure 5 shows the hysteresis loop of the nanowires at 5 K. All measured curves are qualitatively similar in the low temperature range of 5–300 K. However, the coercive field measured in these nanostructures has been found to depend on temperature, as shown in Fig. 6. The observation of coercive field at temperatures below T_M supports that in this temperature range the antiferromagnetic structure of the nanowires core coexists with a ferrimagnetic phase. Such phase would be related to the previously mentioned miscompensation of magnetic moments in the nanowires surface. Above the Morin temperature, the nanowires become weakly ferromagnetic, and the antiferromagnetic-magnetic coupling, as well as the coercive field, decreases. In the hysteresis

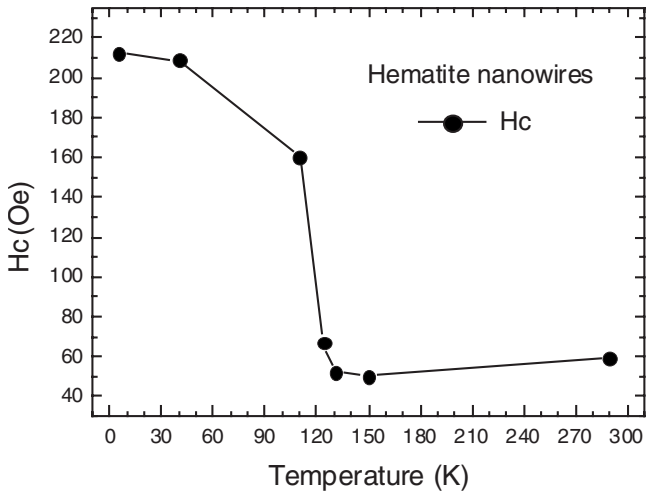

FIG. 6. Temperature dependence of the coercive field for α-Fe_2O_3 nanowires in the 5–300 K range (line is just a guide to the eye).

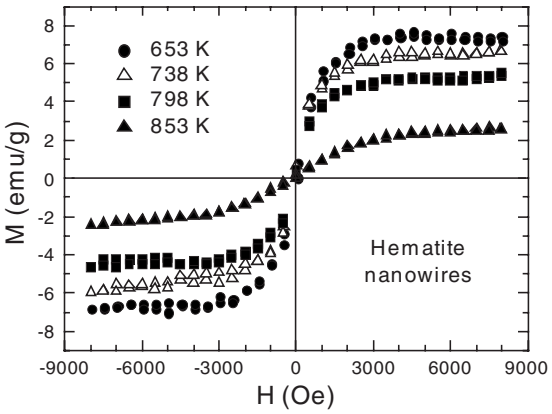

FIG. 7. Hysteresis loops for the hematite nanowires measured at several temperatures below T_N.

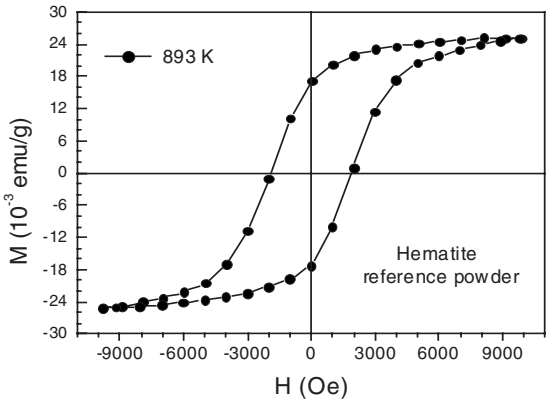

FIG. 8. Hysteresis loop for the hematite reference powder at 893 K.

loops of the bulk powder, coercive field appears only above T_M, 262 K, showing that below this temperature the material is antiferromagnetic. Hysteresis loops of the nanowires at different temperatures up to T_N are shown in Fig. 7. Coercive fields and remanence are negligible at all temperatures. In agreement with the M(T) curves, an abrupt decrease in magnetization by reaching the T_N value is observed. A hysteresis loop of the reference powder at 893 K with coercive field (1900 Oe) and remanence is shown in Fig. 8. Similar loops with different H_C and remanence values are observed at temperatures below the Néel temperature. All magnetic measurements can be understood considering the nanowires formed by two different regions: an antiferromagnetic core, with properties similar to that of bulk hematite but lower transition temperature, surrounded by a ferrimagnetic shell with transition temperature slightly lower that the Néel temperature of the core.

IV. CONCLUSIONS

Single-crystal α-Fe_2O_3 nanowires grown by a thermal evaporation-deposition method, with diameters of about 100–200 nm and lengths of up to 10 μm, present a magnetic behavior different from that of bulk material in powder form. While bulk material presents the usual transitions at 262 and 960 K, transitions for nanowires occur at lower temperature values—123 K for T_M and 852 K for T_N. In addition to these differences in transition temperatures, which are common in nanosized materials, some other magnetic features have been observed. M(T) curves measured in nanowires show another, less marked, transition at 738 K and a higher magnetization than in the reference powder. Coercive field has been measured below T_M in the nanowires, where the bulk material presents a pure antiferromagnetic behavior. The results can be phenomenologically explained assuming the nanowires being composed of two different coexisting phases: an antiferromagnetic core and a ferrimagnetic shell. This ferrimagnetic shell would be responsible of the higher magnetic signal and of the coercivity observed in the temperature range below T_M, where no ferromagneticlike behavior is expected.

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