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Exchange bias in single-crystalline CuO nanowires

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Exchange anisotropy has been observed and investigated in single-crystalline CuO nanowires grown by thermal oxidation of Cu. The exchange bias field decreases by increasing temperature and can be tuned by the strength of the cooling field. A training effect has also been observed. The obtained results can be understood in terms of a phenomenological core-shell model, where the core of the CuO nanowire shows antiferromagnetic behavior and the surrounding shell behaves as a spin glass-like system due to uncompensated surface spins. © *2010 American Institute of Physics*. [doi:10.1063/1.3428658]

One-dimensional (1D) magnetic nanostructures, such as nanowires, nanotubes, and nanobelts, are currently the subject of increasing research because of their huge potential in technological applications related to recording media, spintronics, medicine, and biology.[1,2] In particular, antiferromagnetic transition metal oxide nanostructures are important for data storage and spin-valve devices.[3] The magnetic properties of such nanostructures usually differ from those of their bulk counterparts due to surface and size effects. The surface actually leads to a breaking of the sublattice pairing in the antiferromagnet and thus to uncompensated surface spins and the appearance of a net magnetic moment. As the size of the magnetic system decreases, the significance of the surface spins increases. Temperature dependent magnetic effects of the surface spins lead to several interesting phenomena, including exchange bias (EB).[3,4] The exchange coupling at a ferromagnetic (FM)/antiferromagnetic (AFM) interface may induce unidirectional anisotropy in the FM below the Néel temperature (T_N) of the AFM, shifting the hysteresis loop along the field axis.[4] EB has been also observed in systems involving FM materials and spin glasses (SG).[3,4] This phenomenon has been investigated mainly in thin films[5,6] and, to a lesser extent, in nanoparticles.[7,8] Only very recently, EB has been reported in certain 1D nanostructures.[9,10]

Cupric oxide (CuO) is not only an AFM transition metal oxide (T_N=230 K) but also a narrow band gap semiconductor (E_g=1.3 eV at room temperature). Due to such dual semiconducting-magnetic properties, it is considered a relevant material for applications including gas sensors, catalysis, field emitters, electrochemical cells, and magnetic storage media.[11–13] In this work, we report on the magnetic properties of single-crystalline CuO nanowires grown by thermal oxidation of Cu. Exchange bias is observed below a blocking temperature of about 19 K. The cooling field and temperature dependences of the EB field (H_{eb}), as well as training effects, have been investigated. The obtained results are interpreted in terms of an AFM nanowire core surrounded by a SG-like shell associated to uncompensated surface spins.

The nanowires were grown using Cu powder (Sigma-Aldrich, 99.99% pure) as starting material. Disk-shaped pellets were prepared by compacting this powder under a compressive load of 5 ton. The pellets were then annealed at 380 °C for 14 h in a horizontal tube furnace under air flow. Such treatment led to the growth of a high density of CuO nanowires, which covered uniformly the surface of the pellets, without the use of a catalyst or a foreign substrate. The structure and morphology of the nanowires were investigated by x-ray diffraction (XRD), using a Philips X'Pert PRO diffractometer, scanning electron microscopy (SEM), using a FEI Inspect S microscope, and high-resolution transmission electron microscopy (HRTEM) using a field emission Jeol JEM 3000F microscope operating at 300 kV. The chemical composition of the grown nanowires was assessed by energy dispersive x-ray microanalysis (EDX). The magnetic characterization of the samples was performed using a superconducting quantum interference magnetometer. The nanowires were easily detached from the mentioned pellets avoiding any contact with metallic tools. Extreme care was actually taken during the whole sample preparation process in order to avoid spurious magnetic signals.[14] Each sample consists of a high amount of nanowires, typically 12–15 mg. Measurements were performed on four CuO samples with fully reproducible results.

A SEM image of the grown nanowires is shown in Fig. 1(a). The average width of the nanowires is 65 nm and the average length 5.5 μm. The relative standard deviations of the nanowire width and height were about 15% and 25%, respectively. All the peaks found in the XRD patterns from these nanostructures [Fig. 1(b)] can be indexed to the CuO monoclinic structure (JCPDS card 048–1548). The high structural quality of the nanowires is supported by HRTEM observations. Figure 1(c) shows a low magnification image of a 70 nm wide nanowire and the corresponding selected area electron diffraction (SAED) pattern. Figure 1(d) shows a high-resolution micrograph of the same nanowire. The interlayer distances measured in the image, 0.275 nm and 0.250 nm are, respectively, consistent with those of the (110) and (002) planes in the CuO monoclinic structure. These measurements reveal the single-crystalline nature of the obtained nanowires. Moreover, extended defects such as twins—frequently observed in CuO nanostructures grown by thermal oxidation of Cu in air[15]—were not found in HRTEM observations of our samples. In addition, no elements other than copper and oxygen were detected by EDX microanalysis.

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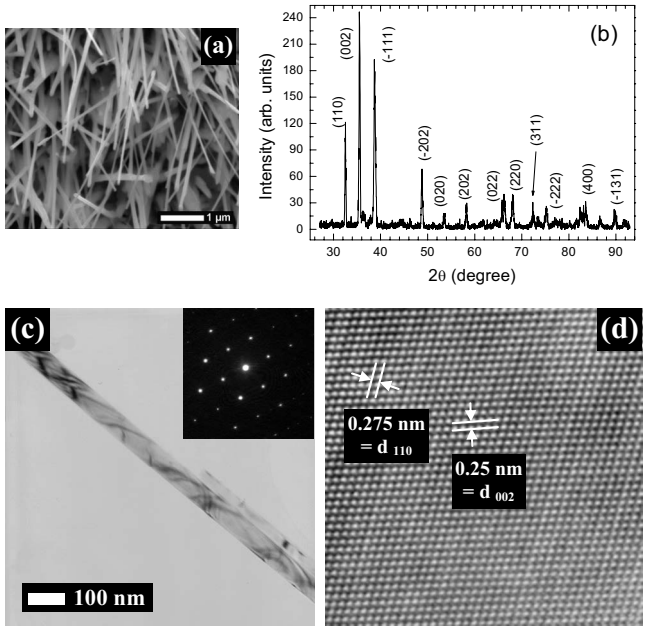

FIG. 1. SEM image (a) and XRD pattern (b) of CuO nanowires grown at 380 °C for 14 h. (c) TEM micrograph of a single-crystal CuO nanowire. The inset shows the corresponding SAED pattern. (d) HRTEM image of the same nanostructure showing the (110) and (002) interplanar distances of this material.

The temperature dependence of the magnetization M(T) under an applied magnetic field of 500 Oe was measured after field cooling (FC) and zero field cooling (ZFC). For FC measurements, the sample was cooled from room temperature under an applied field of 10 kOe. Representative results are shown in Fig. 2. The ZFC curve shows a clear maximum at $T_B \sim 19$ K and an evident separation from the FC curve below T_B, suggesting a SG-like behavior at low temperatures.[9,10,16] Such behavior can be attributed to uncompensated surface spins in the nanowires, which result frozen due to the applied field. In our case, T_B is much lower than T_N. This effect is thought to be partially related to the thickness of the AFM phase. If such thickness is smaller than a system dependent critical dimension of the AFM, the Néel temperature of the AFM is substantially reduced. Other size effects are caused by the fact that the anisotropy of the AFM depends on its dimensions. If we assume that the AFM anisotropy decreases as its size is reduced, a reduction in T_B would be expected.[3,4]

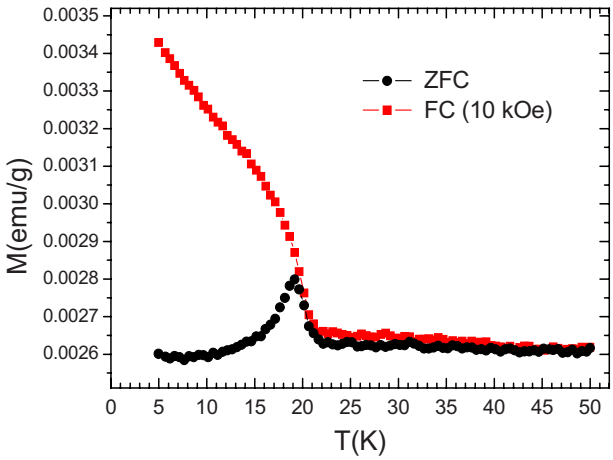

FIG. 2. (Color online) ZFC and FC magnetization curves measured in an applied field of 500 Oe as a function of temperature. The cooling field was 10 kOe.

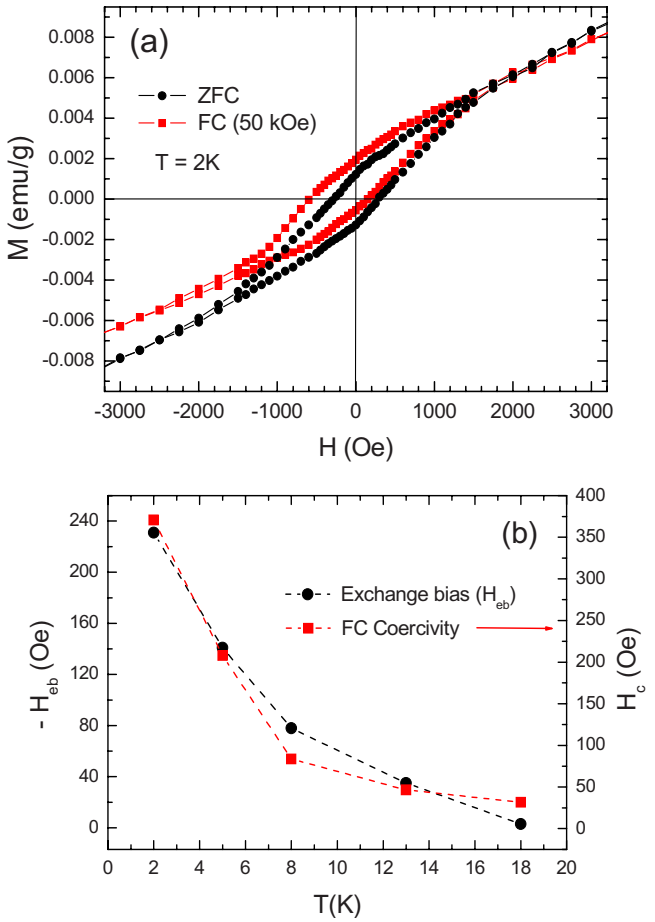

FIG. 3. (Color online) (a) ZFC and FC hysteresis loops of the CuO nanowires at 2 K. (b) Temperature dependence of the FC coercive field (H_{FC}) and the exchange bias field (H_{eb}). Dashed lines are guides to the eye.

Hysteresis loops of the CuO nanowires recorded at 2 K under ZFC, and ZFC conditions are shown in Fig. 3(a). For FC loops, the sample was cooled from room temperature under an applied field of 50 kOe. The loop recorded under ZFC conditions is symmetrical, centered about the origin and exhibits a coercive field of about 270 Oe. On the contrary, the FC hysteresis loop shows a shift toward negative magnetic fields as well as an enhanced coercivity (~370 Oe at 2 K). Furthermore, a significant vertical shift in the loop toward positive magnetization values is also appreciated. All these features are indicative of an EB effect and can be explained, as discussed below, on the basis of a phenomenological core-shell model where the core of the CuO nanowire shows AFM behavior and the surrounding shell posses a net magnetic moment due to a high number of uncompensated surface spins. Similar models have been used in order to explain the magnetic properties of other oxide nanowires.[9,10] The exchange coupling present at the interface between the AFM core and the magnetic shell induces a unidirectional anisotropy in the latter layer. The strength of this anisotropy is measured by the exchange bias field (H_{eb}), defined as $H_{eb}=(H_{c1}+H_{c2})/2$, where H_{c1} and H_{c2}, respectively, represent the left and right coercive fields. The value of $|H_{eb}|$ decreases by increasing temperature from 230 Oe at 2 K to zero at temperatures very close to the so-called[3] blocking temperature T_B, indicating that the interface magnetic inter-

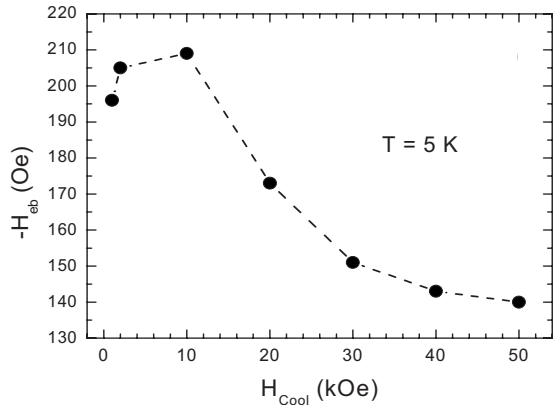

FIG. 4. Exchange bias field as a function of the cooling field measured at 5 K (line is a guide to the eye).

actions are no longer detectable. In addition, the FC coercivity increases below T_B, [Fig. 3(b)], which is probably linked to a small anisotropy of the AFM core. In the case of exchange biased systems containing an AFM with small anisotropy, when the FM rotates it drags the spins irreversibly, hence increasing the FM coercivity.[4]

Concerning the nature of the magnetic shell surrounding the AFM core of the nanowires, other features besides the shape of the M(T) curves suggest a SG-like behavior of the surface spins. For instance, the hysteresis loop at 2 K appears still open in fields up to 2 kOe [Fig. 3(a)], which is frequently observed in others SG-like systems.[10] Traces of the hysteresis are closed loops for applied fields of about 2.5 kOe [Fig. 3(a)] while saturation is observed for applied field values of about ±11000 Oe, indicating that the reported shifts are not related to a minor loop effect.[10,17] The vertical shift in magnetization is related to the presence of interfacial spins remaining pinned along the cooling field direction. A positive (upward) shift is usually attributed to a FM interface coupling.[18,19] Another common feature of the EB system is the training effect, which describes the decrease in H_{eb} when the sample is successively field cycled at a fixed temperature. Systems with AFM thin layers or small grains exhibit much larger training effects,[3] which are expected to appear enhanced in nanostructured materials. To study such effect, the nanowires were cooled in 50 kOe from room temperature to 5 K and six hysteresis loops were recorded. A moderate reduction in H_{eb} was measured between the first and the second loops, where H_{eb} falls by ~15%. After six loops H_{eb} was found to decrease by ~25%.[17] This training effect can be associated with instability of the spin structure, which leads to a reduction in magnetization after repetitive hysteresis cycles. Such effect supports the assumption of a SG-like surface with multiple spin configurations, when a rearrangement of the surface spins is present after each magnetization reversal.

Figure 4 shows that the magnitude of H_{eb} can be tuned by the cooling field (H_{cool}). We found that H_{eb} increases with increasing H_{cool} up to about 10 kOe and then decreases for higher H_{cool} values. This behavior is similar to that found in some granular systems containing AFM and FM nanoparticles,[20,21] although it has not been reported for CuO nanoparticles[7] and differs from that observed in Co_3O_4 nanowires, where H_{eb} raised for increasing H_{cool}.[9] A strong influence of H_{cool} on the EB phenomenon may be expected due to the multivalley energy structure and multiple equivalent spin configurations of the SG-like phase. In the FC process, a preferred configuration is imposed upon the SG-like surface spins. According to the H_{cool} value, the magnetization of the ordered phase tends to align more and more in the field direction. As the temperature is lowered across T_B, a spin configuration of the SG-like phase will be selected through the exchange interaction with the ordered component. Hence, depending on H_{cool}, the degeneracy of the SG state can be reduced. Actually, strong enough magnetic fields can destroy the SG-like state entirely.[18,21] This may explain why H_{eb} decreases for strong H_{cool} fields. The possibility of effectively tuning the exchange bias field of the nanowires by modifying the cooling field is of special interest for applications in spintronics, where CuO nanowires are also of interest due to spin-dependent quantum transport effects.

In summary, EB has been observed and investigated in single-crystal CuO nanowires grown by thermal oxidation of Cu. The effect is appreciated below a blocking temperature of ~19 K. The EB field decreases by increasing temperature or the number of consecutive FC loops, and can be tuned by the strength of the cooling field. The obtained results are interpreted in terms of an AFM nanowire core surrounded by a SG-like shell associated to uncompensated surface spins.

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