Exchange Bias in Cr_2O_3/Fe_3O_4 Core/Shell Nanoparticles

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We report the exchange bias in antiferromagnet/ferrimagnet Cr_2O_3/Fe_3O_4 core/shell nanoparticles. The magnetic field hysteresis curve for Cr_2O_3/Fe_3O_4 nanoparticles after field-cooling (FC) clearly showed both horizontal ($H_{EB}\sim 610$ Oe) and vertical ($\Delta M\sim 5.6$ emu/g) shifts at 5 K. These shifts disappeared as the temperature increased toward the Neel temperature of Cr_2O_3 ($T_N\sim 307$ K). The H_{EB} and ΔM values were sharply decreased between the 1st and the 2nd magnetic field cycles, and then slowly decreased with further cycling. These results are discussed in terms of the formation of single domains with pinned, uncompensated, antiferromagnetic spin and their evolution into multi-domains with cycling.

Keywords : exchange bias, Cr_2O_3/Fe_3O_4, core/shell nanoparticles, pinned uncompensated antiferromagnetic domain

1. Introduction

The discovery of magnetic hysteresis loop shifts in field-cooled Co/CoO nanoparticles [1] has raised research interest in an exchange bias (EB) due to its scientific interest and potential applications [2]. The EB occurs in ferromagnet/antiferromagnet composites, in which the Curie temperature (T_C) of ferromagnet is higher than the Neel temperature (T_N) of the antiferromagnet, and strongly depends on the interface characteristics [3-5].

Numerous experiments have been performed on magnetic multilayers [6, 7], such as Fe/Cr, and on core/shell-type nanoparticles with the same transition metal [8], such as Co/CoO, because of the fundamental importance in spin valves, tunneling devices, and ultra-high density recording media. However, only a few reports have been published on core/shell-type nanoparticles composed of different transition metals [9, 10], probably due to the difficulty in synthesis. Since the transition metal oxides show complicated magnetic structures with large variations of T_N and T_C [11, 12], the combination of various materials as the core and shell may facilitate tuning the strength of the EB field (H_{EB}). In addition, since the interface size and strain can be controlled by varying the core size and material, respectively, we may be able to gain a deeper understanding of the EB phenomena.

In this paper, we report our on-going research on the EB in Cr_2O_3/Fe_3O_4 core/shell nanoparticles. At 5 K, the magnetic hysteresis loop clearly shows both horizontal and vertical shifts, as well as a training effect. The dependences of H_{EB} and vertical shift on temperature and cycling are quite similar. This suggests that the pinned, uncompensated, antiferromagnetic spin near the interface plays a role in the EB of Cr_2O_3/Fe_3O_4.

2. Experiments

Core/shell-type Cr_2O_3/Fe_3O_4 nanoparticles were prepared by the conventional sonochemical method [13]. To make the Cr_2O_3 core, the pellet form of Cr_2O_3 was synthesized by a solid-state reaction method and then crushed into the powder form of Cr_2O_3 by ball-milling for 15 days. After the Cr_2O_3 powders were thoroughly dispersed in a reaction vessel, ultrasonic waves (20 kHz, 750 W) were applied for 1 hour along with a supply of reaction ($FeSO_4\dot{i}7H_2O$ and CH_3COOH) and oxidation (NH_4OH and $NaNO_2$) solutions. The obtained powders were filtered and then dried at 60 °C for 24 hours.

The core/shell structure and particle size were examined by a combination of scanning electron microscopy (SEM) and dynamic light scattering analysis. The phase and crystalline quality were characterized by X-ray diffraction (XRD) using Cu $K\alpha$ radiation. The magnetic hysteresis loops were obtained by using the vibrating sample magnetometer (VSM) option in a physical property measure-

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ment system (Quantum Design, PPMS).

3. Results and Discussion

Fig. 1 shows the XRD pattern of the Cr_2O_3/Fe_3O_4 core/shell nanoparticles. In the selected diffraction angles, the two peaks corresponded to Cr_2O_3 (104) and Fe_3O_4 (311). A wide range scan of the diffraction pattern (data not shown) revealed the absence of any other crystalline phases. By using the Scherrer formula, we estimated the grain size of Cr_2O_3 and Fe_3O_4 as 35 nm and 20 nm, respectively.

Probably due to the ball-milled Cr_2O_3 core, the shape and size of the Cr_2O_3/Fe_3O_4 core/shell nanoparticles were not uniform. The SEM image (the left inset of Fig. 1) of Cr_2O_3/Fe_3O_4 reveals the presence of several shapes, such as ellipsoid and bar, with sizes ranging from 100 to 300 nm. The particle size distribution is presented in the right inset of Fig. 1. Despite wide size distribution of Cr_2O_3 (solid bars) and Cr_2O_3/Fe_3O_4 (open bars), we roughly estimated their average diameters as 70 nm and 170 nm, respectively. In combination with the XRD result, we considered that two or three layers of the 20-nm-sized Fe_3O_4 grains were stacked on Cr_2O_3 in our Cr_2O_3/Fe_3O_4 core/shell nanoparticles.

Fig. 2 shows the magnetic hysteresis loop of the Cr_2O_3/Fe_3O_4 core/shell nanoparticles at 5 K after the field-cooling (FC) under H=30 kOe from 350 K. The clearly

Fig. 2. Field-cooled magnetic hysteresis curves of the Cr_2O_3/Fe_3O_4 nanoparticles for the 1st (solid line) and the 10th (dashed line) cycles at 5 K. The inset shows the changes of H_{EB} (open circles) and ΔM (closed circles) with cycling.

unsymmetrical hysteresis loop exhibits an EB behavior. The loop shifts horizontally to the left side with a negative H_{EB} of 610 Oe and also vertically upward with a vertical shift ΔM of 5.48 emu/g. Here, H_{EB} is defined as $H_{EB} = -(H_{c,L}+H_{c,R})/2$, where $H_{c,L}$ and $H_{c,R}$ are the left and right coercive fields, respectively, while ΔM is defined as $\Delta M=(M_{r,U}+M_{r,D})$, where $M_{r,U}$ and $M_{r,D}$ are the up and down remanent magnetizations, respectively. The existence of DM clearly implies the presence of a pinned, uncompensated, antiferromagnetic spin near the core/shell interface due to FC.

The exchange biased hysteresis loop of the Cr_2O_3/Fe_3O_4 nanoparticles shows strong magnetic field cycling dependences, which indicates the training effect [2]. As clearly shown in Fig. 2, the magnetic hysteresis loop of the 10th cycle (a dashed line) is different from that of the 1st cycle (a solid line), and becomes more symmetrical through decreasing $H_{c,L}$ and $M_{r,U}$. [The changes of $H_{c,R}$ and $M_{r,D}$ during cycling are quite small.] The inset of Fig. 2 shows the changes of H_{EB} and ΔM according to cycle number. Significant reductions of H_{EB} and ΔM occur between the 1st and the 2nd cycles. After the 3rd cycle, the H_{EB} and ΔM values decrease smoothly with further cycling. Similar to the explanation for the Co/CoO bilayers [14], the training effect in the Cr_2O_3/Fe_3O_4 nanoparticles may be explained by the fact that the FC induces the formation of a thin, uncompensated, antiferromagnetic single domain, which can be destroyed upon the first magnetization reversal, and then transformed into stable multi-domains.

Fig. 3 shows the magnetic hysteresis loops of the Cr_2O_3/Fe_3O_4 core/shell nanoparticles at selected temperatures
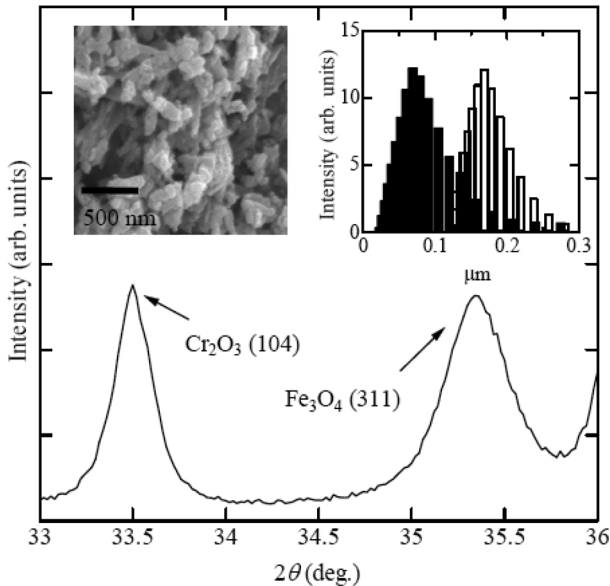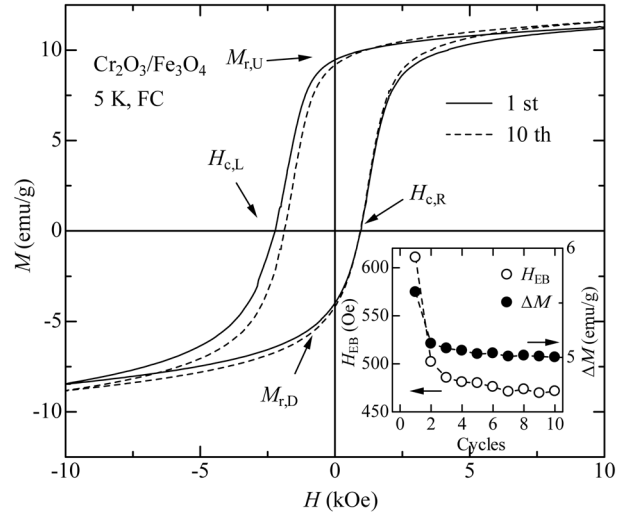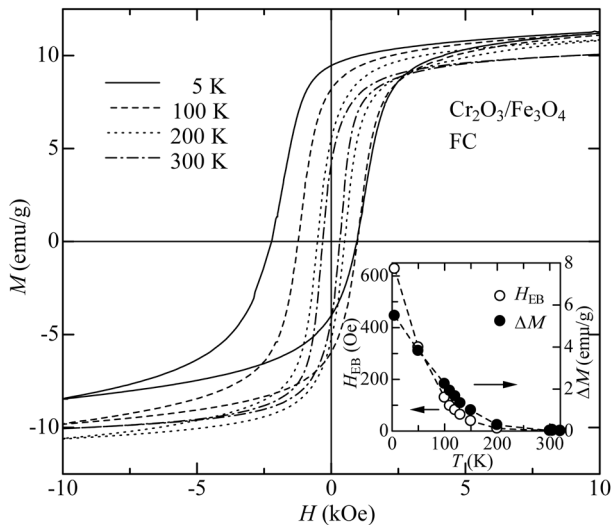

Fig. 1. X-ray diffraction pattern of the Cr_2O_3/Fe_3O_4 nanoparticles at selected angles. The left and right insets present the scanning electron microscope image and the particle size distributions (solid bars: Cr_2O_3, open bars: Cr_2O_3/Fe_3O_4), respectively.

Fig. 3. Temperature-dependent magnetic hysteresis curves of the Cr_2O_3/Fe_3O_4 nanoparticles. The inset shows the changes of H_{EB} (open circles) and ΔM (closed circles) with temperature.

after the FC under H=30 kOe from 350 K. The exchange-biased hysteresis loop at 5 K is significantly affected by the increasing temperature, and then changes into an unbiased loop near 300 K. The inset of Fig. 3 shows the temperature dependences of H_{EB} (open circles) and ΔM (solid circles). The H_{EB} and ΔM values rapidly decrease with increasing temperature and then finally disappear near 307 K, which corresponds to the blocking temperature T_B. According to the temperature dependence of the magnetization data (data not shown) and published literature values [15], T_N of Cr_2O_3 is reported to be 307 K, which coincides with T_B. Although further investigation is needed for confirmation, the coincidence of T_N with T_B was attributed to the large grain size of our Cr_2O_3 nanoparticles [16].

4. Conclusion

Antiferromagnet/ferrimagnet Cr_2O_3/Fe_3O_4 core/shell nanoparticles clearly showed an EB below the T_N of Cr_2O_3. The EB field (H_{EB}~610 Oe) and vertical shift (ΔM~5.6 emu/g) were observed in this system. The origin of these shifts and the detailed exchange coupling near the interface are under investigation.

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