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Proteresis in Co:CoO core-shell nanoclusters

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The magnetism of ultrasmall Co:CoO core-shell nanoclusters is investigated. The structures, produced by cluster-beam deposition, have Co core sizes ranging from 1 to 7 nm and a CoO shell thickness of about 3 nm. Hysteresis loops as well as zero-field-cooled and field-cooled magnetization curves have been measured and a striking feature of the nanostructures is the existence of proteretic (clockwise) rather than hysteretic loops in the core-size range from 3 to 4 nm. The proteretic behavior and its particle-size dependence reflect a subtle interplay between various anisotropies and exchange interactions in the Co and CoO phases and at the Co–CoO interface. © 2008 American Institute of Physics. [DOI: 10.1063/1.2829239]

I. INTRODUCTION

Since the discovery of unidirectional anisotropy more than 50 years ago,¹ the Co:CoO system has attracted continuing attention. A poorly understood aspect is the occurrence of inverted hysteresis loops or *proteresis*. Such loops, found in some nanostructures with competing magnetic interactions,² are cycled clockwise, in contrast to ordinary or anticlockwise hysteresis loops. This is different from loops shifted horizontally or vertically due to exchange bias, and from constricted hysteresis loops, also known as wasp-shaped or butterfly loops. Proteretic loops are encountered, for example, in pharmacodynamics, where one plots the effect of a drug as a function of the drug concentration.³ Similar effects occur in transport systems such as superconductors.⁴ In magnetism, they are counterintuitive, because the clockwise character of the loops indicates the production rather than dissipation of magnetic energy. The reason for the occurrence of magnetic proteresis is the involvement of competing interactions, especially exchange.

Inverted loops were originally obtained and qualitatively explained in granular thin films.² Recent advances in cluster processing^{5,6} have provided the basis for structuring nanoparticles with well-defined and narrow size ranges. The phenomena considered in this paper share distant relationships with the exchange coupling in hard-soft nanocomposites^{7–9} and with exchange bias.^{1,10} The former phenomenon exhibits some similarities, such as a size-dependent exchange coupling to a soft phase, but it does not involve competing exchange interactions. The latter has the same physical origin, namely, the interplay between ferromagnetic and antiferromagnetic exchanges, but maps these interactions on a simple exchange field.

Here we produce Co:CoO core-shell clusters and investigate the magnetism of the nanostructures, with particular reference to magnetic proteresis in surface-modified nanoclusters, which are an emerging research field with potential

applications in areas such as ultrahigh-density magnetic recording, magnetoresistive sensors, contrasting agents in medicine, and catalysis.^{11–13}

II. SAMPLE PREPARATION AND CHARACTERIZATION

Nearly monodisperse Co nanoclusters having sizes from 1 to 7 nm were produced in a cluster-beam deposition system, as described, for example, in Ref. 14. The core-shell clusters were then produced by partial oxidation in an oxygen atmosphere of fixed flow rate before they were deposited into a silica matrix to form pseudomultilayers. To avoid intercluster interactions, we have focused on dilute pseudomultilayers with a nominal cluster-layer thickness of 1 Å in a silica matrix of thickness 15 nm. However, for comparison, we have also produced dense-packed series. Figure 1 shows the schematic structure.

The formation of uniform Co:CoO core-shell clusters of various sizes is confirmed by transmission electron microscopy (TEM) (Fig. 2). While the core-shell particles are too small for phase analysis using x-ray diffraction, the oxidation of Co is known to yield CoO,^{15,16} and the corresponding core-shell structure is consistent with our magnetic measurements. In contrast to CoO, other oxides such as Co₂O₃ and Co₃O₄ require high oxygen flow rates, as explained in Ref. 17. With relatively low oxygen flow rate other oxide is not expected in our samples. The Co core is in the fcc phase, as concluded from the x-ray diffraction examination of bare and

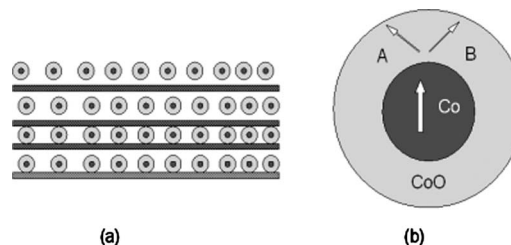


FIG. 1. Geometry of Co:Co core-shell nanostructures: (a) pseudomultilayer and (b) core-shell particle with A and B showing sublattice magnetizations in CoO.

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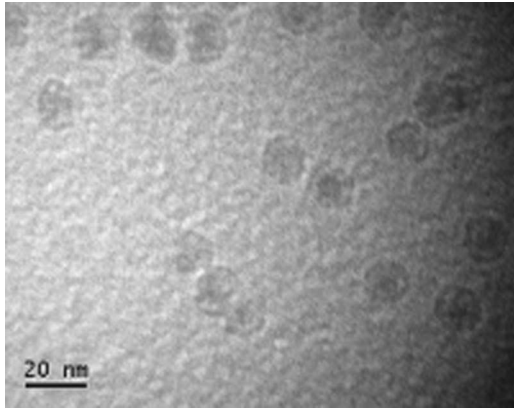


FIG. 2. TEM image of core-shell clusters having a CoO shell thickness of 3 nm and Co core diameters of 7 nm.

unoxidized clusters. Note that variable oxygen flow rates could lead to different oxidation degrees and shell thicknesses, but in the present work, oxygen flow rate was fixed to ensure that the structures have a common shell thickness of about 3 nm. High resolution TEM analysis of clusters made with the same method in the past¹⁷ suggests that the CoO shell consists of nanocrystallites in the cubic (NaCl-type) crystal structure.

III. MAGNETIC PROPERTIES

The magnetic properties of the clusters were measured using the superconducting quantum interference device in the temperature range from 5 to 300 K. $M(H)$ loops and magnetizations after both zero-field cooling and field cooling were measured. We have also performed atomic force microscopy and magnetic force microscopy imaging on the silica-embedded core-shell structures, but the resolution of the images (not shown in this paper) is insufficient to study individual core-shell clusters.

The zero-field-cooled (ZFC) and field-cooled (FC) magnetizations were obtained in a standard way, and the blocking temperature T_p is estimated from the peak (or maximum) of the ZFC curve. Figure 3(a) shows the FC and ZFC curves for 7 nm core-shell clusters and Fig. 3(b) gives the dependence of the blocking temperature on the core diameter D . The experimental data are reasonably well reproduced by a phenomenological power law, $T_p \sim D^2/V_s^{3/2}$, solid line in (b), where V_s is the volume of the CoO shell. The quadratic dependence on D indicates that the core-shell interface plays an important role. This does not necessarily imply substantial interface anisotropy. A more likely explanation is that the

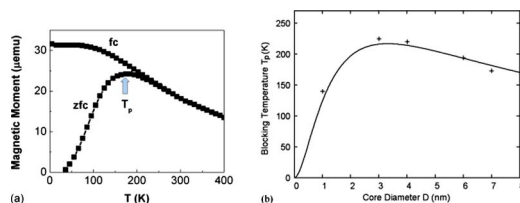


FIG. 3. (Color online) Blocking behavior of the core-shell structures: (a) ZFC and FC magnetization curves for 7 nm clusters, and (b) blocking temperature T_p as a function of core diameter. The solid curve in (b) is a model prediction.

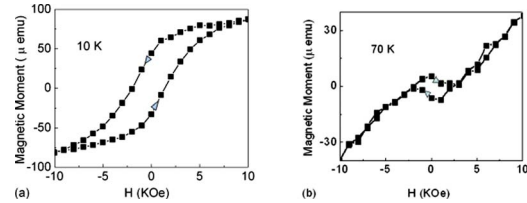


FIG. 4. (Color online) Magnetization curves for (a) $D=1$ nm (hysteresis) and (b) $D=3$ nm (proteresis).

relatively soft Co couples to adjacent CoO regions (crystal-lites) and that the CoO volume involved in this coupling is proportional to the interface area.

The pronounced decrease of T_p with increasing size may have two reasons. First, the CoO is nanocrystalline (x-ray amorphous) rather than single crystalline, which leads to some random-anisotropy averaging in the CoO scaling as $1/V_s^{1/2}$. Note that random-anisotropy averaging is well known in ferromagnets¹⁸ but also occurs in antiferromagnets, where it becomes visible near spin-flop transitions¹⁹ or, in the present, by exchange coupling to a ferromagnet. Second, the coupling due to the Co core is strongest for neighboring CoO grains, so that more distant grains are effectively decoupled. A more detailed discussion of the $T_p(D)$ dependence is difficult, because V_s and D are strongly coupled and the shell thickness D is difficult to tune. For example, small D leads to the formation of CoO islands on the Co surface, which affects the above-mentioned random-anisotropy argument.

Depending on the core diameter, the $M(H)$ loops are clockwise (proteretic) or anticlockwise (hysteretic). Proteretic loops are observed in a certain core-size window, from about 3 nm to about 4 nm. Figure 4 shows typical loops for different core sizes.

The densely packed samples exhibit vertical loop shifts, in addition to the more common horizontal exchange bias. This could be understood by the strengthening of the CoO shell due to contact among the core-shell clusters, thus enhancing the magnitude of exchange coupling. Combination of vertical and horizontal shifts produces a “rotating” behavior with increasing temperature. Both shifts have the same origin and can be considered as inner loops from a micro-magnetic point of view, but they complicate the quantitative understanding of the $M(H)$ loops. Shown in Fig. 5 are the rotating loops and the temperature dependence of vertical shift.

IV. DISCUSSION AND CONCLUSIONS

Clockwise hysteresis or proteresis, as shown in Fig. 4(b), is much less common than ordinary hysteresis, which is char-

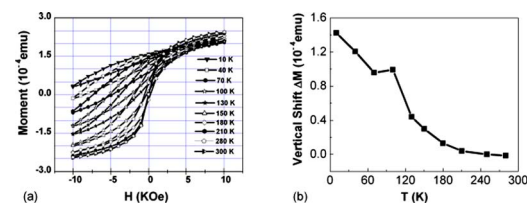


FIG. 5. (Color online) Temperature dependence of hysteresis loops (a) and vertical shifts (b) of compact films.

acterized by counterclockwise $M(H)$ loops. Since clockwise or inverted loops produce rather than dissipate magnetic energy, the phenomenon is somewhat counterintuitive, indicating that the magnetic energy is outweighed by other energy contributions, such as interatomic exchange. A semiquantitative explanation of clockwise hysteresis loops in granular ferromagnetic/antiferromagnetic (FM/AFM) composites has been given by O'Shea and Al-Sharif.² The essence of the explanation is that the external or Zeeman field changes the sublattice magnetizations A and B in Fig. 1(b). The Co magnetization wants to follow the Zeeman field, too, but it is also coupled to the CoO sublattices, and the switching of the CoO magnetizations A and B may actually overcompensate the Zeeman interaction and switch the Co magnetization in the opposite direction. In more detail, the explanation involves three types of exchange, namely, (i) the predominantly AFM intra- and intersublattice exchange in the CoO, (ii) the ferromagnetic exchange in the Co, and (iii) the Co/CoO interfacial exchange, which competes with the AFM exchange of the CoO. The magnetocrystalline magnetic energy required for proteresis is largely provided by the CoO phase.

Of course, this explanation is rather general and applies to broad range of FM/AFM structures.^{2,20} What is the reason for the window ($2 \text{ nm} < D < 5 \text{ nm}$) where the effect occurs in the Co:CoO core-shell structures? To explain the size dependence, we first consider soft ferromagnetic regions (inclusions) in a hard but ferromagnetic matrix. The hard and soft regions are strongly exchange coupled when the dimension of the soft region does not exceed a few nanometers.^{7,21} Replacing the anisotropic ferromagnetic matrix by an anisotropic antiferromagnetic matrix complicates the micromagnetism of the system but leaves the involved length scales unchanged. In both cases, very *small* length scales lead to nearly complete effective exchange coupling, and the magnet behaves like a single hysteretic unit. Only on a length scale of a few nanometers, where the involved interactions are of comparable strength, does one observe proteresis.

In summary, proteresis (clockwise hysteresis) is observed in Co:CoO core-shell particles. The phenomenon is limited to Co core sizes from about 3 to 4 nm—cores smaller than 3 nm and larger than 4 nm lead to ordinary

hysteresis loops. Proteresis reflects a complicated interplay between ferromagnetic and antiferromagnetic exchange interactions and anisotropies; it is a true nanoscale phenomenon, not occurring in atomic-scale and macroscopic magnets. Future research is necessary to quantify this intriguing size dependence.

ACKNOWLEDGMENTS

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