Enhancement of magnetic coercivity and macroscopic quantum tunneling in monodispersed Co/CoO cluster assemblies

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Magnetic properties have been measured for monodisperse-sized Co/CoO cluster assemblies prepared by a plasma-gas-condensation-type cluster beam deposition technique. The clear correlation obtained between exchange bias field and coercivity suggests the enhancement of uniaxial anisotropy owing to the exchange coupling between the ferromagnetic Co core and antiferromagnetic CoO shell, and magnetic disorder at the core–shell interface. A nonthermal magnetic relaxation observed below 8 K, being referred to as macroscopic quantum tunneling of the magnetization, is ascribed to the enhanced uniaxial anisotropy. © *1999 American Institute of Physics.* [S0003-6951(99)02150-6]

Using a plasma-gas-condensation (PGC)-type cluster beam deposition apparatus, we have succeeded in preparing monodispersed Co clusters with the mean sizes $d = 6-15$ nm and the standard deviation less than 10% of d.[1] In this size range, Co clusters reveal a characteristic percolation during the assembling process.[2] Next, we have tried to oxidize Co cluster surface uniformly, because the melting point of CoO is so high to stabilize the cluster surface. In the core-shell type Co/CoO monodisperse cluster assemblies thus obtained, a tunnel-type conductivity and enhanced magnetoresistance between the Co clusters are prominent in the Coulomb blockade regime, being well separated from the high temperature regime dominated by the conduction of the semiconducting CoO layers.[3] In this article, we describe another tunneling behavior in the magnetic relaxation of the monodispersed Co/CoO cluster assemblies, which is attributable to the enhanced magnetic coercivity.

Unidirectional exchange anisotropy (UEA) was first discovered by Meiklejohn and Bean[4] in compacted oxide-coated Co particles and attributed to an exchange coupling between the ferromagnetic (FM) Co core and the antiferromagnetic (AF) CoO layers. The typical UEA effect is a marked shift of the hysteresis loop against the applied field, commonly referred to as an exchange bias field, H_{ex}, when field cooling the system from temperatures above the Néel temperature T_N of the AF to $T < T_N$. The related phenomena have been extensively studied theoretically[5–8] and experimentally,[9–12] because they are technologically important, i.e., domain stabilizers in magnetiresistive heads[13] and spin-valve based devices.[14] The first simple model[4] dealt with the unidirectional anisotropy by the assumption of a perfect uncompensated plane of the AF at the interface and predicted H_{ex} which was two orders of magnitude larger than those observed. Mauri *et al.*[5] provided an explanation for the reduction of H_{ex}: the formation of a domain wall parallel to the interface dramatically lowers the energy required to reverse the magnetization. Alternatively, Koon[7] predicted a correct value for H_{ex} as a result of a perpendicular orientation between the FM and AF axis directions, similar to the classical spin-flop state in bulk AF. A recent experiment of polarized neutron diffraction has shown that exchange coupling between the Co and CoO layers is apparently responsible for the increased projection of the AF moments perpendicular to the cooling field direction.[12] The theoretical models mainly focused on explaining the unidirectional anisotropy and obtaining the correct order of H_{ex} but predicted no effect on the coercivity H_c, although the shifted hysteresis loop is always accompanied by an enhancement of the coercivity, which is much larger than the intrinsic value of the FM core or layer.[4,15] Quite recently, Schulthess and Butler[8] have made a calculation for CoO/FM films using an atomistic Heisenberg model and have shown that there are two coupling mechanism at work, the spin-flop coupling (being responsible for a large coercivity) and FM–AF coupling through uncompensated defects (accounting for exchange bias field). It can be considered, however, that for small CoO-coated Co clusters, because of single-domain structure of Co core grains and the small size of cores and shell crystallites, reversal mechanism and real roughness at core–shell interface are different from that for simple FM/AF bilayer.

The samples were prepared by the PGC-type cluster beam deposition apparatus.[1,3] The electron diffraction pattern clearly indicated coexistence of face-centered cubic (fcc) Co and CoO phases, while the high resolution transmission electron microscope image displayed that the Co clusters were covered with the CoO shells consisted of very small crystallites.[3] Magnetic measurements for samples formed on a polyimide film were performed at room temperature using a superconducting quantum interference device magnetometer between 4.2 and 400 K with the maximum field of 50 kOe.

Hysteresis loops were measured at 5 K both after zero field cooling (ZFC) and field cooling (FC) the samples from 300 to 5 K in a magnetic field, H, of 20 kOe. The direction of H used to measure the loops was parallel to that of the cooling field. The inset of Fig. 1 shows the ZFC and FC loops of the Co/CoO monodispersed cluster assembly with $d = 6$ nm prepared at $R_{O_2} = 1$ sccm. For this sample, the thickness of

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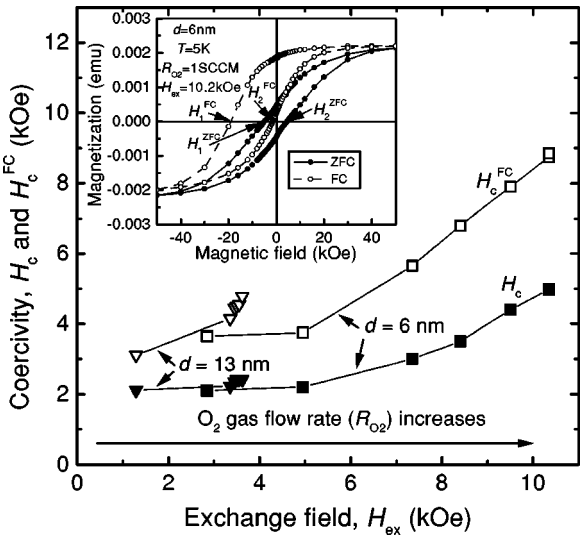

FIG. 1. Coercivities, H_c and H_c^{FC} of the ZFC and FC samples at 5 K as a function of the exchange bias field H_{ex} for the Co/CoO monodispersed cluster assemblies with $d=6$ and 13 nm prepared at different R_{O_2}. The inset shows hysteresis loops of the zero-field-cooled (ZFC) and field-cooled (FC) Co/CoO monodispersed cluster assembly with mean cluster size of $d=6$ nm prepared at the O_2 gas flow rate $R_{\mathrm{O}_2}=1$ sccm.

the CoO shell have been estimated to be about 1 nm by direct observation of the high resolution transmission electron microscope, being consistent with the Co core size of about 4 nm estimated from the Langevin fitting of the experimental data above room temperature. Large exchange bias field H_{ex} $(=|H_1^{\mathrm{FC}}+H_2^{\mathrm{FC}}|/2\approx 10\,\mathrm{kOe})$ is detected, which indicates presence of strong UEA in the present specimens. Moreover, a large coercivity H_c $(=|H_1^{\mathrm{ZFC}}-H_2^{\mathrm{ZFC}}|/2 \approx 5\,\mathrm{kOe})$ is also detected for the ZFC case in which the UEA effect is randomized. This H_c value is much larger than that of Ag-coated Co particles (500–2000 Oe for $d=5-13\,\mathrm{nm}$).[15] It is hard to imagine that such enhancement of H_c results from magnetic interaction among the clusters in ferromagnetic cluster assemblies. In addition, the low field thermomagnetic curves show the following distinct features. The ZFC magnetization is almost zero but the FC magnetization was unchanged below 150 K because of the strong exchange coupling between the Co core and CoO shell. Both ZFC and FC magnetization curves rapidly increase with temperature and reveal a maximum at $T_{\max}=230\,\mathrm{K}$. These behaviors indicate that UEA rapidly decreases above 150 K, which is consistent with our experimental results (not shown here): the loop shift vanishes above a critical temperature $T_v=190\,\mathrm{K}$, where T_v is much lower than the Néel temperature ($T_N=293\,\mathrm{K}$). A similar result observed for oxide passivated Co fine particles was attributed to the superparamagnetic behavior of the antiferromagnetic oxide shell with very small crystallites above a blocking temperature (150 K).[15] However, taking into account the roughness of core–shell interfaces as well as the small sizes of the Co cores and CoO shell crystallites, the sharp cusps in both ZFC and FC magnetization curves should be related to the properties of a spin disorder state at and near core–shell interface, similar to a spin glass. In order to further examine the origin of these effects, we measured the dependence of the position of the cusp (at freezing T_f) on the frequency of the alternating-current (ac) field because the frequency shift in T_f can offer a good criterion for distinguishing a spin-glass-like material from a superparamagnet. Our experimental result (not shown here) indicates that T_f depends on the frequency of the ac field and the peak is shifted to the low temperature direction with decreasing the frequency of measurement. When the frequency varies between $\omega=1000$ and 1 Hz, T_f is reduced by about 10%: $\Delta T_f/[T_f\Delta(\log\omega)]$ is about 0.03. These values are the same order as those of the spin glasses and smaller than the values of the superparamagnets.[16]

Figure 1 shows coercivities, H_c and H_c^{FC} $(=|H_1^{\mathrm{FC}}-H_2^{\mathrm{FC}}|/2)$, of the ZFC and FC samples at 5 K as a function of H_{ex} for the monodispersed Co/CoO cluster assemblies with $d=6$ and 13 nm prepared at different R_{O_2}. Both H_c and H_c^{FC} increase with the increase in H_{ex}, indicating the clear correlation between H_{ex} and H_c. The value of H_c^{FC} is about twice as large as that of H_c at a given H_{ex} value. This suggests that a magnetization reversal mechanism of rotation and a uniaxial anisotropy are compatible with UEA. Although there is microscopically UEA in a ZFC single-domain particle system with a ''perfect'' core–shell interface, it is macroscopically smeared out by the random orientation of the single-domain cores.[4] Finite H_{ex} and no increase in H_c^{FC} are expected when the field cooling is performed across the Néel temperature of the AF shell. However, the small Co cores, small CoO shell polycrystallites, and their interface roughness lead to frustration and a disordered state in the FM and AF phases close to the interfaces, similar to spin glass.[17,18] Recently, H_{ex} and H_c have been discussed for the parmalloy/CoO bilayers[19,20] as a theoretical extension of Malozemoff's model.[6] The UEA effect is interpreted in terms of random exchange fields due to interface roughness and inperfection between the FM and AF, giving the correct order of magnitude for H_{ex}. The enhancement of H_c was attributed to pinning of the domain walls in the FM layer by local-energy minima created by the random interaction field with the AF layer. H_{ex} is not sensitive to the AF layer thickness, while H_c markedly increase with decreasing the FM layers.[20] In Fig. 1, the size reduction of the Co core is more important for the increase in H_c although the increase in H_{ex} can be correlated with both the increase in the CoO layer thickness and the decrease in the Co core size. In this context, the magnetic anisotropy is ascribed to the magnetic disorder at the core–shell interface. If we similarly express the magnetic anisotropy energy as a Fourier polynomial series, we can allocate the unidirectional and uniaxial components of the magnetic anisotropy energy to the odd and the even terms, respectively.[19]

The magnetic relaxation phenomenon of macroscopic quantum tunneling (MQT) is another characteristic in small magnetic particle systems.[21–23] The crossover temperature from a thermal activation regime to a quantum tunneling regime, T_c^*, theoretically scales with the magnetic anisotropy constant of the materials.[24] The MQT effect is observable at experimentally accessible temperatures only for materials with high uniaxial anisotropy. In the present Co/CoO monodispersed cluster assemblies, since a large uniaxial exchange anisotropy is induced at low temperature, we expect MQT of magnetization.

Magnetic relaxation measurements were performed for the Co/CoO cluster assembly using the following procedure:

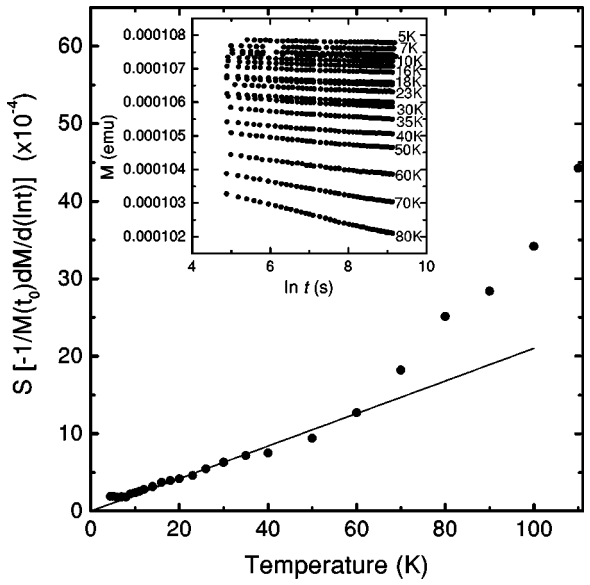

FIG. 2. Magnetic viscosity, S, as a function of temperature for the Co/CoO monodispersed cluster assembly with $d=6$ nm prepared at $R_{O_2}=1$ sccm. The inset shows time dependence of magnetization at different temperatures.

first the sample was cooled from 300 K to a lower temperature in low magnetic field, $H_a=100$ Oe; the field was then reversed to $H_b=-100$ Oe and the variation of the magnetization with time was measured at this temperature. As shown in the inset of Fig. 2, the magnetic relaxation follows logarithmic time dependence:[25]

$$M(t)=M(t_0)[1-S(T)\ln(t/t_0)], \tag{1}$$

where S is the magnetic viscosity and t_0 the fitting parameter. There is no single exponential time dependence expected for isolated ferromagnetic cluster systems. This implies the wide distribution of the anisotropy energy which is ascribed to the polycrystalline CoO and the interface roughness in spite of the well-monodispersed cluster size distribution. By least square fitting of Eq. (1) to the results in the inset of Fig. 2, the S value is estimated as a function of temperature and shown in Fig. 2. The temperature variation of S at a high temperature range deviates from linearity. However, for $8<T<50$ K, S varies linearly with T, extrapolating to zero when $T=0$, as would be expected for the magnetic relaxation via thermal activation. This indicates that the interaction between the Co cores is smaller than the energy barrier height, probably because the bare dipole interaction between the Co cores is shielded partially by the AF CoO shell. The other remarkable feature is that the S values are independent of temperature at $T\leqslant 8$ K. This suggests the presence of MQT of magnetization in the CoO-coated Co cluster assembly. Taking into account $H_c=5$ kOe (see Fig. 1), we estimated the uniaxial anisotropy constant, $K\approx H_c\times M_c\approx 7.2\times 10^6$ erg/cm^3 which is larger than the bulk value ($K=4.5\times 10^6$ erg/cm^3 and 2.5×10^6 erg/cm^3 for a hexagonal-close packed (hcp) and fcc structure, respectively).[26] Therefore, the high character temperature of $T_c^*=8$ K is ascribed to the enhanced uniaxial unisotropy due to exchange coupling between the FM Co core and AF CoO shell.

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