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## Exchange Anisotropy of Monodispersed Co/CoO Cluster Assemblies

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Monodispersed Co/CoO cluster assemblies with the mean cluster size of 13 nm have been prepared using a plasma-gas-condensation-type cluster beam deposition apparatus. The structural analysis and magnetic measurement indicate that the Co cluster is covered by an oxide shell composed of CoO. The effect of the oxygen gas flow rate during deposition and that of temperature on the coercivity and hysteresis loop shift induced by field cooling were measured. The effect of the CoO shell on the loop shift and the temperature dependence of the exchange anisotropy are discussed. The unidirectional anisotropy is negligible above 200 K for the present assemblies. This is ascribed to the rapid decrease of the anisotropy of the antiferromagnetic interfacial layers near the interface of the Co cores and CoO shells.

KEYWORDS: unidirectional exchange anisotropy, Co/CoO cluster assembly, Monodispersivity, loop shift, enhanced coercivity

### 1. Introduction

Unidirectional exchange anisotropy (UEA) was discovered in field-cooled Co/CoO particles<sup>1)</sup> more than 40 years ago. It is caused by the strong exchange coupling between the ferromagnetic (FM) Co core and the antiferromagnetic (AF) CoO layer. A typical UEA effect is the marked shift of the hysteresis loop against the applied field, commonly referred to as a loop shift,  $\Delta H_c$ , when field cooling the system from temperatures above the Néel temperature  $T_N$  of the AF to  $T < T_N$ . Related phenomena have been studied theoretically<sup>2-5)</sup> and experimentally,<sup>6-12)</sup> because they are technologically important to domain stabilizers in magnetoresistive heads<sup>13)</sup> and spin-valve-based devices.<sup>14)</sup> However, the physical origin of the UEA has not been well explained. The first simple model<sup>1)</sup> on the unidirectional anisotropy was based upon a perfect uncompensated plane of the AF at the interface, and predicted  $\Delta H_c$  which was two orders of magnitude larger than the observed ones. Mauri *et al.*<sup>2)</sup> provided an explanation for the reduction of  $\Delta H_c$ : the formation of a domain wall parallel to the interface markedly lowers the energy required to reverse the magnetization. Alternatively, Koon<sup>4)</sup> predicted a correct value for  $\Delta H_c$  as a result of using a perpendicular orientation between the FM and AF moments, similar to the classical spin-flop state in bulk AF. The theoretical models mainly focused on explaining the unidirectional anisotropy and obtaining the correct order of  $\Delta H_c$ . However, they predicted no effect on the coercivity  $H_c$ , although a shifted hysteresis loop is always accompanied by an enhancement of the coercivity, which is much larger than the intrinsic value of the FM core<sup>1,7)</sup> or layer.<sup>6)</sup> Moreover, for small CoO-coated Co clusters, the reversal mechanism and actual roughness at the core-shell interface are different from that for simple FM/AF bilayers because of the single-domain structure of Co core grains and the small size of cores and shell crystallites.

We have recently constructed a plasma-gas-condensation (PGC)-type cluster beam deposition apparatus<sup>15,16)</sup> based upon both plasma-glow-discharge vaporization and the inert gas condensation technique.<sup>17)</sup> Using this system, we have succeeded in obtaining monodispersed transition metal clusters with the mean size  $d = 6$  to 15 nm and a standard deviation of less than 10% of the mean sizes. The monodispersed

Co/CoO cluster assemblies thus obtained revealed the characteristic tunnel-type conductivity and magnetoresistance effect, arising from the uniform size of Co cores and thickness of CoO shells.<sup>18)</sup> In this paper, we describe the magnetic properties and UEA of the monodispersive Co/CoO cluster assemblies prepared by the PGC-type cluster beam deposition technique. We discuss the effect of the oxide shell composed of a single CoO phase on the loop displacement and the temperature dependence of the UEA effect.

### 2. Experimental

The samples were prepared by the PGC-type cluster beam deposition apparatus. The details of cluster deposition were described elsewhere.<sup>15,16)</sup> We introduced oxygen gas through a nozzle set near the skimmer into the deposition chamber to form cobalt oxide shells covering the Co clusters before deposition on the substrate. This process ensures that all Co clusters are uniformly oxidized before the cluster assemblies are formed.<sup>18)</sup> For constant  $R_{Ar}$  or  $R_{Ar} + R_{He}$ , the gas pressure in the deposition chamber can be adjusted to lower than  $3 \times 10^{-4}$  Torr by changing the flow rate of oxygen gas ( $R_{O_2}$ ). The initial stage of cluster deposition on the microgrids was observed using a Hitachi HF-2000 transmission electron microscope (TEM). The cluster assemblies were formed on a polyimide film at room temperature with the apparent thickness of about 100 nm, as measured using a quartz thickness monitor. Magnetic measurements were performed, using a superconducting quantum interference device with a magnetometer, between 5 and 390 K with the maximum magnetic field of 50 kOe.

### 3. Results

We can control the cluster size by changing  $R_{Ar}$  and  $R_{He}$ . Figure 1 shows (a) a TEM image and (b) an electron diffraction pattern of the oxide-coated Co clusters prepared at  $R_{Ar} = 500$  sccm and  $R_{O_2} = 0.44$  sccm. As shown here, the clusters are almost monodispersed; the mean diameter,  $d$ , is about 13 nm. The electron diffraction pattern clearly indicates the coexistence of fcc Co and CoO phases, while the high-resolution image shows that the Co clusters are covered with the small CoO shell crystallites, namely, they possess a well-defined core-shell-type structure.<sup>18)</sup>

Hysteresis loops were measured at 5 K after zero field cooling (ZFC) and field cooling (FC) the samples from 300 to 5 K

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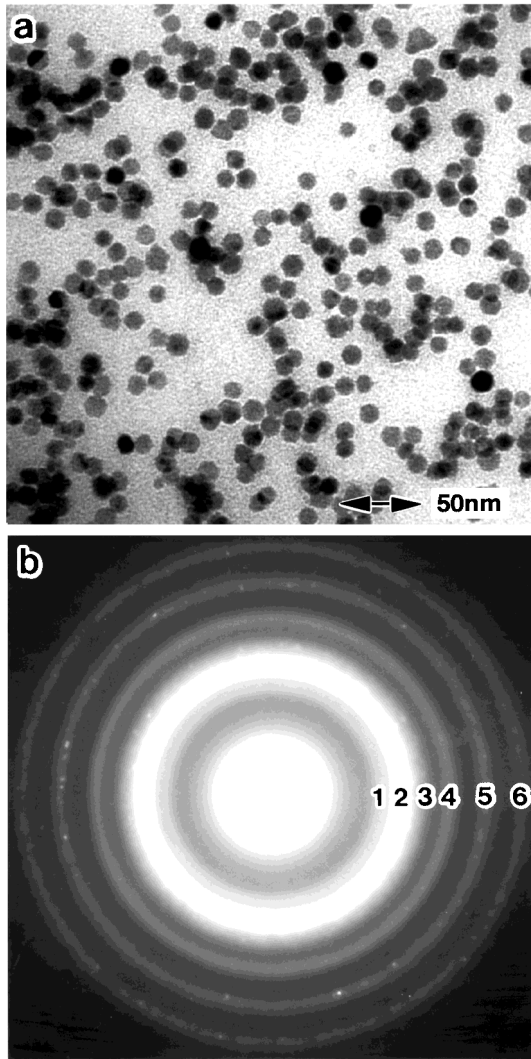


Fig. 1. (a) TEM image and (b) electron diffraction pattern of the initial stage of the CoO-coated Co clusters (with mean cluster diameter of  $d = 13$  nm) prepared on a carbon microgrid at the Ar gas flow rate of  $R_{Ar} = 500$  sccm and the O<sub>2</sub> gas flow rate of  $R_{O_2} = 0.44$  sccm. The diffraction rings: 2, 3, 5 and 6 are for {111}, {200}, {220} and {311} of the fcc-Co phase, respectively, and 1 and 4 for {111} and {220} of the CoO phase, respectively.

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. Figure 2 shows the ZFC and FC loops of the Co/CoO cluster assemblies with  $d = 13$  nm prepared at  $R_{O_2} = 0$  and 1 sccm. For the sample with  $R_{O_2} = 1$  sccm, a large loop shift along the opposite direction of the cooling field is detected in the FC loop, while a symmetric feature is obtained in the ZFC loop (the loop shift  $\Delta H_c = H_c^{ZFC} - H_c^{FC}$ , where  $H_c^{ZFC}$  and  $H_c^{FC}$  are indicated by arrows in Fig. 2(b)). This confirms the presence of the UEA due to the strong exchange coupling between the FM Co core and the AF CoO shell. For  $R_{O_2} = 0$  sccm [Fig. 2(a)], the shift appears but it is much smaller than that for  $R_{O_2} = 1$  sccm [Fig. 2(b)]. This is due to partial oxidation of the cluster assembly by exposing it only to the ambient atmosphere.

Figure 3 shows the coercivity,  $H_c$ , and  $\Delta H_c$  as a function of  $R_{O_2}$  for the Co/CoO cluster assemblies with  $d = 13$  nm.  $\Delta H_c$  initially increases with increasing  $R_{O_2}$  and then becomes constant above  $R_{O_2} = 1$  sccm, probably because the oxida-

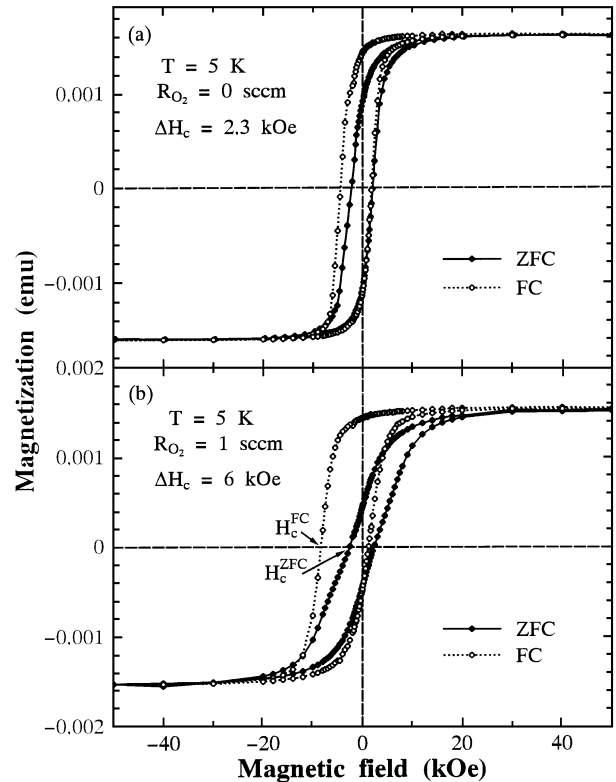


Fig. 2. Hysteresis loops of the zero-field-cooled (ZFC) and field-cooled (FC) Co/CoO cluster assemblies with the mean cluster size of  $d = 13$  nm prepared at the O<sub>2</sub> gas flow rate  $R_{O_2}$  of (a) 0 sccm and (b) 1 sccm.

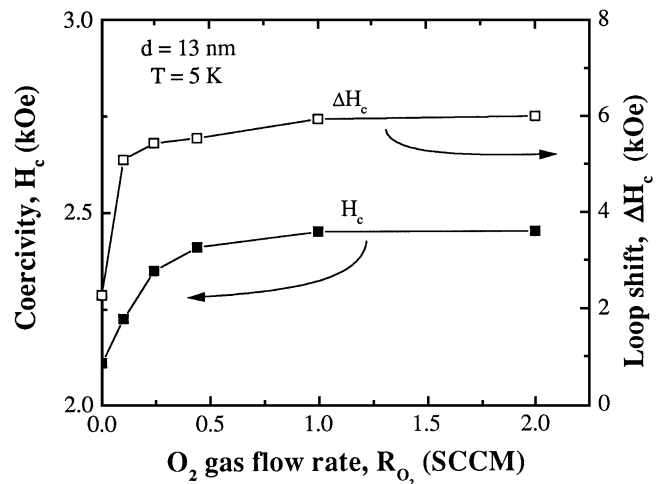


Fig. 3. Coercivity,  $H_c$ , and loop shift,  $\Delta H_c$ , as a function of the O<sub>2</sub> gas flow rate,  $R_{O_2}$ , for the Co/CoO cluster assemblies with  $d = 13$  nm.

tion does not progress any further and has reached a stable state for  $R_{O_2} > 1$  sccm in the low-O<sub>2</sub>-pressure atmosphere ( $< 3 \times 10^{-4}$  Torr). Moreover, it should be noted that  $H_c$  also rapidly increases with increasing  $R_{O_2}$ , up to about 2.5 kOe at  $R_{O_2} = 1$  sccm. This  $H_c$  value is larger than that of Ag-coated Co particles (500–2000 Oe for  $d = 5$ –13 nm).<sup>7)</sup> These results clearly suggest that the exchange interaction plays an important role in the increase of  $H_c$  and  $\Delta H_c$  because the volume fractions of the FM Co cores and AF CoO shells change with  $R_{O_2}$ . Recently,  $\Delta H_c$  and  $H_c$  have been discussed with respect to the Permloy/CoO bilayers<sup>12)</sup> as a theoretical extension of Malozemoff's model.<sup>3)</sup> The UEA effect is interpreted in terms

of random exchange fields due to interface roughness and imperfection between the FM and AF, to give the correct order of magnitude for  $\Delta H_c$ . The enhancement of  $H_c$  was attributed to the pinning of the domain walls in the FM layer by local-energy minima created by the random interaction field with the AF layer.

Figure 4 shows (a) the reduced saturation magnetization,  $M_s(T)/M_s(5\text{ K})$ , (b)  $H_c$  and (c)  $\Delta H_c$  as a function of temperature for the Co/CoO cluster assemblies with  $d = 13\text{ nm}$  prepared at  $R_{O_2} = 0, 0.44, 1$  and  $2\text{ sccm}$ . The  $M_s(T)/M_s(5\text{ K})$  values for all the samples slightly decrease with increasing temperature, and the decreasing rate increases with increasing  $R_{O_2}$ .  $H_c$  monotonically decreases with increasing temperature for  $R_{O_2} = 0\text{ sccm}$ , while  $H_c$  does not change markedly below  $100\text{ K}$  and decreases rather rapidly with increasing temperature above  $100\text{ K}$  for  $R_{O_2} = 0.44, 1$  and  $2\text{ sccm}$ . The  $H_c$  values at  $300\text{ K}$  for  $R_{O_2} = 0.44, 1$  and  $2\text{ sccm}$  are smaller than that for  $R_{O_2} = 0\text{ sccm}$ . Such a temperature dependence clearly indicates an effect of the degree of oxidation. For  $R_{O_2} = 0\text{ sccm}$ , the Co cluster assemblies were prepared without introducing oxygen gas, and were only partially oxidized when exposed to the ambient atmosphere. Thus, the

amount of oxide is very small and the exchange interaction is weaker than those in the Co/CoO cluster assemblies prepared with  $R_{O_2} > 0\text{ sccm}$ , leading to a large difference in  $H_c$  between  $R_{O_2} = 0$  and  $>0\text{ sccm}$  in a low temperature range. At  $300\text{ K}$ , on the contrary,  $H_c$  for  $R_{O_2} = 0\text{ sccm}$  is larger than that for  $R_{O_2} > 0\text{ sccm}$ . This crossover of  $H_c$  for  $R_{O_2} = 0$  and  $R_{O_2} > 0\text{ sccm}$  is interpreted as follows. In the present study, the initial Co cluster size is controlled at about  $13\text{ nm}$  and the CoO layer thickness increases with increasing  $R_{O_2}$ . In other words, the effective size of the FM Co cores is larger for  $R_{O_2} = 0\text{ sccm}$  than  $R_{O_2} > 0\text{ sccm}$ . At  $300\text{ K}$ , the CoO shells become paramagnetic because of  $T_N = 293\text{ K}$  for bulk CoO. Then, the effective magnetic anisotropy energy which suppresses the superparamagnetic thermal fluctuation is larger for the samples prepared with  $R_{O_2} = 0\text{ sccm}$  than those with  $R_{O_2} > 0\text{ sccm}$ , causing a difference in  $H_c$ . As seen in Fig. 4(c),  $\Delta H_c$  also depends on  $R_{O_2}$ . For  $R_{O_2} = 0\text{ sccm}$ ,  $\Delta H_c$  is not zero but is not as large as that for  $R_{O_2} > 0\text{ sccm}$ . For  $R_{O_2} > 0\text{ sccm}$ ,  $\Delta H_c$  rapidly decreases with increasing temperature and disappears at about  $T_v = 200\text{ K}$ , where  $T_v$  is much lower than the Néel temperature of the bulk CoO, being dependent on the degree of surface oxidation. 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 ( $150\text{ K}$ ).<sup>7)</sup> The superparamagnetism of small AF particles is associated with uncompensated surface spin. However, as discussed in §4, the disappearance of the loop shift above  $200\text{ K}$  for the CoO-coated Co cluster assemblies is due to the spin disorder at or near the core-shell interface.

#### 4. Discussion

Compared with the oxide-passivated Co fine particles<sup>7)</sup> prepared by the vapor deposition technique, in which the oxide shell is composed of  $\text{Co}_3\text{O}_4$  and CoO phases, the effective temperature range of the unidirectional exchange anisotropy is different in the present Co/CoO cluster assemblies. We measured the loop shift by the following two different cooling procedures. 1) Specimens were cooled in a zero field from  $300\text{ K}$  to a temperature  $T_i$ , and further cooled in  $H = 20\text{ kOe}$  from  $T_i$  to  $10\text{ K}$  at which the magnetic hysteresis loops were measured; 2) specimens were cooled in  $H = 20\text{ kOe}$  from  $300\text{ K}$  to a temperature  $T_f$ , and further cooled in a zero field from  $T_f$  to  $10\text{ K}$  at which the magnetic hysteresis loops were measured. Figure 5 shows the measured  $\Delta H_c$  for the sample with  $d = 13\text{ nm}$  prepared at  $R_{O_2} = 1\text{ sccm}$  as a function of temperatures  $T_i$  and  $T_f$ . In curve (a),  $\Delta H_c = 0.5\text{ kOe}$  for  $T_i = 30\text{ K}$ , and is only about 10% of the largest shift ( $\Delta H_c = 5.3\text{ kOe}$ ) for  $T_i > 200\text{ K}$ , while in curve (c) (from ref. 7),  $\Delta H_c \approx 3.09\text{ kOe}$  even for  $T_i = 30\text{ K}$ , and is almost 95% of the largest shift for  $T_i > 200\text{ K}$  as well as insensitive to  $T_i$ . Moreover, in curve (b),  $\Delta H_c$  does not depend on  $T_f$  for  $T_f \leq 50\text{ K}$  and rapidly decreases with increasing  $T_f$  for  $T_f > 50\text{ K}$ , while in curve (d) (from ref. 7), it monotonically decreases with increasing  $T_f$ . These differences in the change of  $\Delta H_c$  with  $T_i$  and  $T_f$  between the present oxide-coated Co cluster assemblies and the samples in ref. 7 clearly indicate that in the former, the oxide shells consist of CoO and in the latter, they are composed of CoO and  $\text{Co}_3\text{O}_4$ , where  $\text{Co}_3\text{O}_4$  has a much lower Néel temperature than the bulk  $\text{Co}_3\text{O}_4$  (about  $40\text{ K}$ ). In addition, it is noteworthy that in

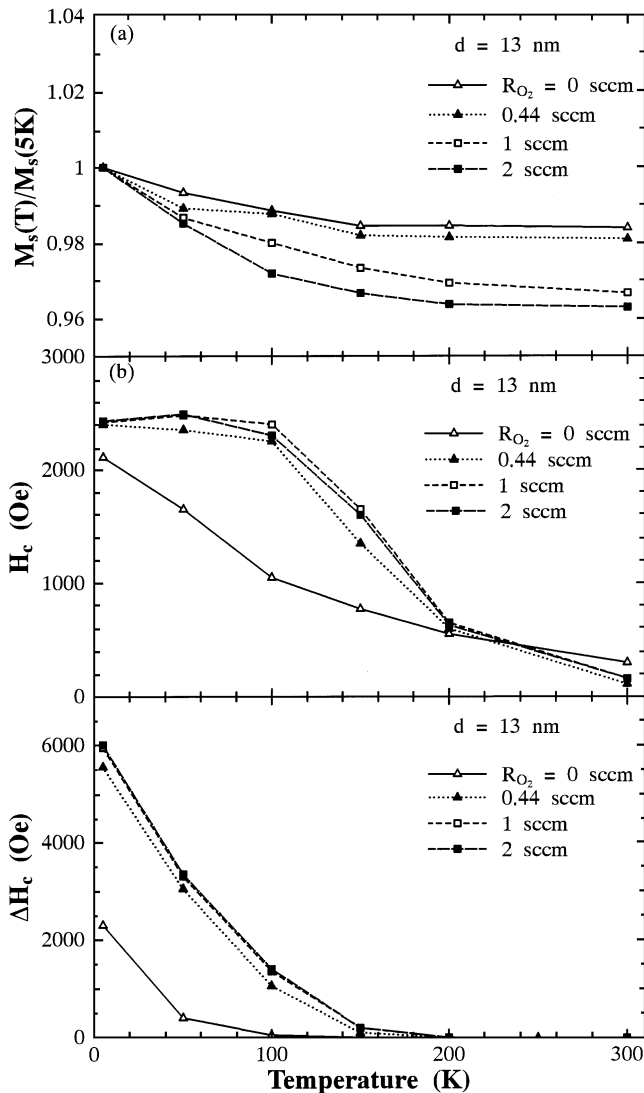


Fig. 4. Temperature dependence of (a) reduced saturation magnetization,  $M_s(T)/M_s(5\text{ K})$ , (b)  $H_c$  and (c)  $\Delta H_c$  for the Co/CoO cluster assemblies with  $d = 13\text{ nm}$  prepared at different  $R_{O_2}$ .

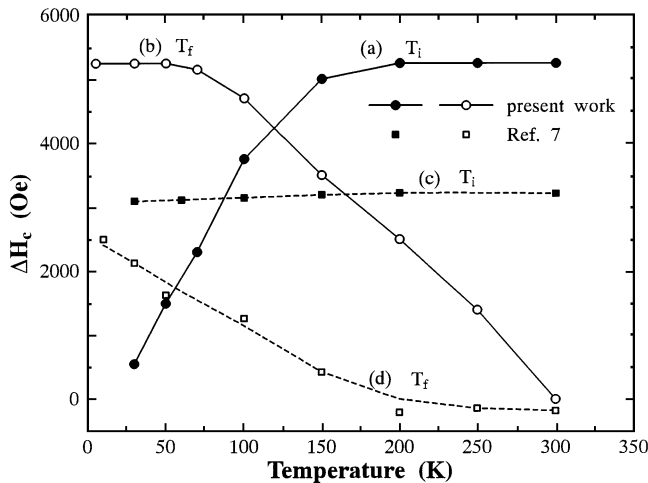


Fig. 5. Loop shift,  $\Delta H_c$ , measured at 10 K. (a) and (b) show the present monodispersed Co/CoO cluster assembly with  $d = 13$  nm prepared at  $R_{O_2} = 1$  sccm; (c) and (d) from ref. 7.  $T_i$  is the temperature at which the field cooling began and  $T_f$  is the temperature at which the field cooling was stopped after being field cooled from 300 K.

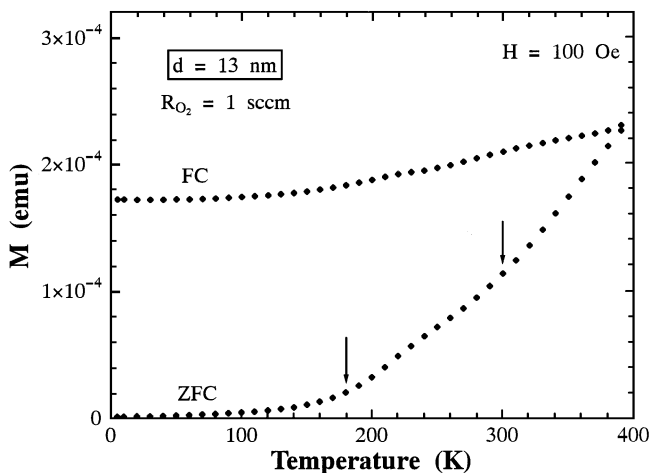


Fig. 6. Low-field thermomagnetic curves,  $M_{ZFC}-T$  and  $M_{FC}-T$ , for the Co/CoO cluster assembly with  $d = 13$  nm prepared at  $R_{O_2} = 1$  sccm.

curve (b),  $\Delta H_c$  is not zero and increases with the decrease of  $T_f$  at  $T_f > 200$  K. This behavior implies the retainment of the exchange anisotropy even at  $T > 200$  K although the loop shift measurements at  $T > 200$  K (Fig. 4) show that  $\Delta H_c$  cannot be detected above 200 K. In order to further examine the effective temperature range of the exchange interaction, we measured low-field thermomagnetic curves,  $M_{ZFC}-T$  and  $M_{FC}-T$ , for the present CoO-coated Co cluster assembly with  $d = 13$  nm prepared at  $R_{O_2} = 1$  sccm (Fig. 6). As seen from Fig. 6, a distinct magnetic cooling effect is observed at low temperatures. The ZFC magnetization is very small and remains almost unchanged below 140 K because of the strong exchange interaction between the Co core and CoO shell. When the temperature is above 140 K, both ZFC and FC magnetizations start to increase. The ZFC magnetization increases more slowly from 180 to 300 K than from 300 to 390 K, indicating that the magnetic anisotropy of the CoO shell is still marked between 200 and 290 K. Considering spin canting<sup>19,20</sup> or spin disorder<sup>21</sup> near the core-shell interface due to the small size of the Co cores and CoO shell

crystallites as well as the spin-flop coupling between the FM and AF moments,<sup>4,5,10</sup> the exchange interaction between the FM core and the AF shell is decreased, leading to the negligible loop shift above 200 K.

## 5. Conclusions

Using the PGC-type cluster beam deposition technique and oxidation process under low pressure ( $< 3 \times 10^{-4}$  Torr), we have obtained monodispersed Co cluster assemblies covered by an oxide shell composed of the single CoO phase. The coercivity and the loop shift strongly depend on the extent of surface oxidation which dominates the exchange coupling between the ferromagnetic Co core and antiferromagnetic CoO shell. The UEA is negligible above 200 K for the present assembly, being ascribed to the rapid decrease of the anisotropy of the AF interfacial layers near the interface of the Co cores and CoO shells.

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