Exchange anisotropy in oxide passivated Co fine particles

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Oxide passivated Co particles have been prepared by vapor deposition in the size range of 50–350 Å. A strong exchange anisotropy was observed due to the core-shell structure of the Co particles, where the core consists of metallic Co and the shell of Co oxides. The exchange anisotropy of the particles was studied using shifted hysteresis loops after the sample was field cooled (FC). The shift in the FC loop exhibited a maximum at a particle size of 80 Å (shift = 10.7 kOe) and is related to the amount of surface oxidation. The shift in the loops disappeared around 150 K in all the samples irrespective of their particle size, and this is attributed to the superparamagnetic behavior of the antiferromagnetic oxide shell.

INTRODUCTION

Exchange anisotropy was discovered by Meiklejohn and Bean[1] in compacted samples of Co particles covered by cobaltous oxide. After their work, a number of studies were performed on Ni-Mn, Co-Mn, Cu-Mn, Ag-Mn, and other alloys[2–6] and a clear evidence of exchange induced anisotropy was shown. The exchange interaction between the moments of the ferromagnetic (F) and antiferromagnetic (AF) regions has been shown[1,7] to give rise to a unidirectional anisotropy when the sample is cooled through the Néel temperature of the antiferromagnet in the presence of a large field. This anisotropy, called exchange anisotropy, can manifest itself in the form of (1) shifted hysteresis loop along the field direction after appropriate field cooling procedures, (2) $\sin\theta$ torque curve, and (3) constant rotational hysteresis at very high fields.

In the present study we report on the exchange anisotropy of oxide covered Co fine particles using displaced hysteresis loops. The effect of particle size, surface oxidation, and temperature on the loop displacement have been studied. The magnetic properties of these particles have been published elsewhere.[8]

EXPERIMENT

Co particles were prepared by the vapor deposition technique.[9] Base pressure of 10^{-5}–10^{-6} Torr was acquired prior to the evaporation of the metal in an inert gas (argon, 99.998% pure) atmosphere. By varying the argon pressure in the 1–30 Torr range, particles in the size range of 50–350 Å were obtained. Particles were collected on a water-cooled Cu plate above the tungsten crucible. Before exposing the powder to the atmosphere, it was passivated with an argon-air mixture for a few hours to obtain the "core-shell" structure. Powders were mixed with molten paraffin wax and stored in quartz capsules for magnetic measurements. Evidence of some further oxidation was observed from the magnetic data,[10] but a stable state was reached after some initial deterioration (10%–20% decrease in magnetization).

The structure and morphology of the samples were studied by x-ray diffraction, selected area diffraction (SAD), and transmission electron microscopy (TEM). Magnetic studies were performed using a superconducting quantum interference device (SQUID) magnetometer in the 10–300 K temperature range and with a maximum field of 55 kOe.

RESULTS AND DISCUSSION

The particles obtained had an fcc structure. The diffraction lines due to oxide were very weak and broad. Magnetic and structural data[8] indicate that the oxides are Co_3O_4 and CoO.

Hysteresis loop measurements on different particle size samples were performed. Loops were measured at 10 K both after zero field cooling (ZFC) and field cooling (FC) the sample from 300 to 10 K in a field of 20 kOe. The direction of field used to measure the hysteresis loop was parallel to that of the cooling field. Figures 1(a) and 1(b) show the ZFC and FC loops of a small and a big particle sample, respectively. ZFC loops are symmetrical about the origin. FC loops are shifted along the applied field direction which signifies the presence of unidirectional exchange anisotropy. For the bigger particles the FC loop only expands towards the applied field direction while in the small particles the loop is both expanded and shifted. The latter behavior is more similar to the Ni-Mn and related alloys where the FC loops are completely displaced from the origin and have positive retentivity in both the hysteresis arms.[5] We define the shift, which is a measure of the exchange anisotropy field as, $H_{c1}^{FC} - H_{c1}^{ZFC}$ [H_{c1} and H_{c2} are marked in Fig. 1(a)]. The other quantity of interest is the displacement of the return arm of the FC loop with respect to the ZFC loop defined as $\Delta = H_{c2}^{ZFC} - H_{c2}^{FC}$. The values of shift and Δ for various samples with different particle sizes are plotted in Fig. 2. Both the shift and Δ are a direct measure of the exchange anisotropy and, hence, of the density of F-AF interfaces and the volume ratio of F to AF phases in the sample. In very small particles (< 80 Å), because of the particle size distribution (which varies approximately from ± 15 Å in smaller particles to ± 50 Å in larger particles), a large fraction of the particles could be completely oxidized. This is because the size of the oxide shell is of the order of 20 Å [from high-resolution TEM
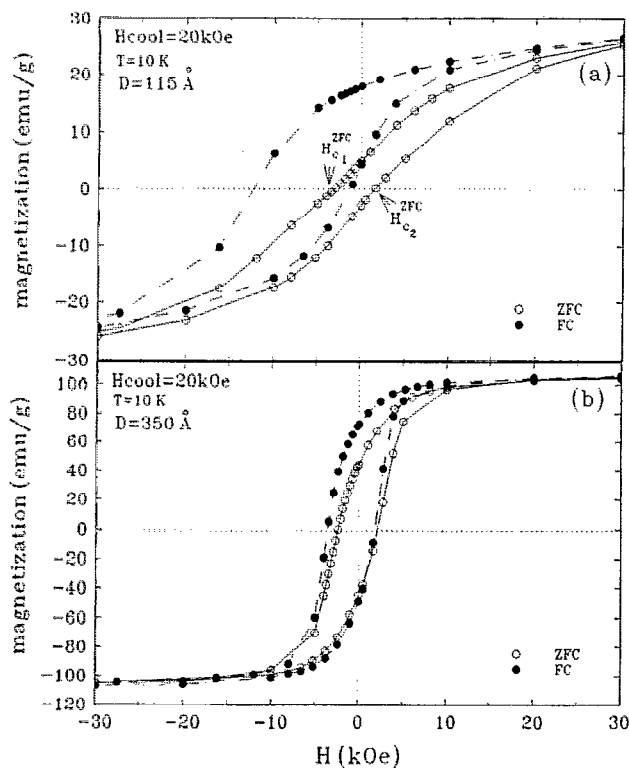
FIG. 1. (a) ZFC and FC loop for a powder of 115 Å particle size, showing a shift of 9.2 kOe in the FC loop. (b) ZFC and FC loop for a powder of 350 Å, showing a shift of only 1.2 kOe.

FIG. 3. Effect of air volume or oxide shell thickness on the shift. The data points are joined by a curve.

(HRTEM)] and, therefore, a 40 Å particle would be expected to be completely oxidized. Such particles will not contribute to the exchange interaction. The higher extent of oxidation in smaller particles is also evident from their smaller magnetization values (Fig. 1 and Ref. 8). For a particle size near 100 Å the volume fraction of the F to AF phases would be comparable and also the density of interfaces would be highest resulting in maximum exchange interaction. As the particle size increases further the volume fraction of the core ferromagnet increases and the interface area with the antiferromagnet decreases resulting in weaker exchange interaction and thus smaller shifts.
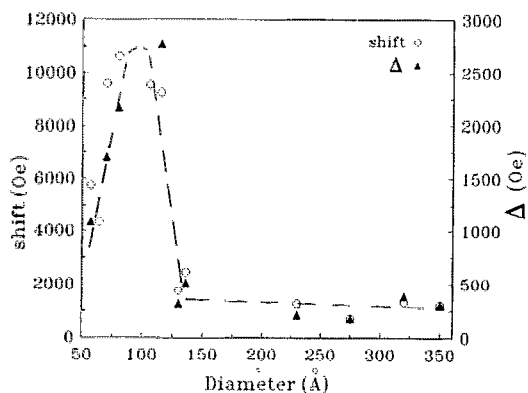
The amount of shift goes through a maximum as the volume of air added for surface passivation is increased (Fig. 3). The particles with no passivation (0 ml of air) are covered with Ag; hence they have a minimal amount of oxide on their surface whereas those with 130 ml of air start to form pure oxide particles; both of these conditions result in small exchange anisotropy and, hence, small shifts. The maximum in the shift is observed near 60 ml of air where the shell thickness has reached an optimum and results in the largest exchange anisotropy. At further oxidation some particles get completely oxidized and do not contribute to exchange anisotropy.

Samples of different sizes were cooled from 300 to 10 K and subsequently warmed and the amount of shift was measured at various temperatures up to 300 K (Fig. 4). The shift, which depends on the coercivity, is very sensitive to oxidation in smaller particles. The data shown in Fig. 4 were taken at different stages of aging in various samples, and therefore the relationship between shift and particle size does not hold anymore. The significance of Fig. 4 is the disappearance of the shift at about 150 K in all the samples irrespective of their particle size. This indicates the loss of exchange anisotropy, which could result from any of the following conditions: (a) the Co-oxide surface coating looses its magnetic order (by reaching its Néel temperature) (b) the Co oxide becomes magnetically soft by be-

FIG. 2. Shift and Δ as a function of particle size, showing a maximum near 80 Å.
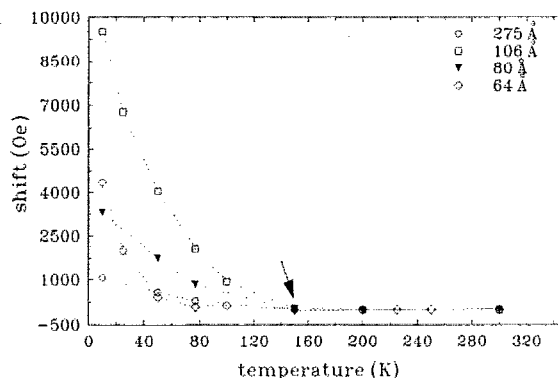

FIG. 4. Effect of temperature on the loop shift. The arrow marks the disappearance of shift in all the samples.

coming superparamagnetic due to its fine crystallite size, (c) the magnetocrystalline anisotropy of Co oxide decreases rapidly at high temperatures, or (d) the Co oxide might be off-stoichiometry and could result in a Néel temperature in between the values for CoO and Co_3O_4. In order to check for the first possibility fine particles of CoO and Co_3O_4 were prepared and their Néel temperature was measured from the peak in the dc susceptibility curves for different particle sizes. A 60 Å CoO powder had a Néel temperature of 270 K (only 20 K less than the bulk CoO) and an 80 Å Co_3O_4 powder had a Néel temperature of 30 K (only 10 K lower than its bulk). The size of the small crystallites of Co oxide found in the surface layer of our Co particles is ~20 Å (observed by HRTEM). It would be hard to imagine that the effect of finite size could reduce the Néel temperature of CoO particles from 270 to 150 K as the size decreases from 80 to 20 Å. Thus the first possibility is ruled out. An estimate of the blocking temperature of a 20 Å CoO particle with a magnetocrystalline anisotropy of 5×10^6 ergs/cc (Ref. 1) is 152 K, which is the temperature where the shift disappears in all of our samples. Thus the superparamagnetism of the oxide shell can explain the loss of exchange interaction in our passivated Co powders. A fast decrease in the crystal anisotropy [condition (c)] could also result in the loss of shifted loop, as has been observed previously in Ag-Mn and Cu-Mn alloys[7] and cannot be ruled out until the temperature dependence of the Co-oxide anisotropy is measured. We also plan to examine condition (d) through XPS measurements to determine the stoichiometry of the Co oxide.

The particle size dependence of shift (Fig. 2) and its temperature dependence (Fig. 4) can also be explained by considering the model proposed by Malozemoff[11] and Mauri *et al.*,[12] where a domain wall is assumed to be formed in the antiferromagnet near the ferromagnetic region.

In order to determine the temperature range where the exchange interaction is effective and also to find which oxide is responsible for this effect, we measured the loop shift by two different cooling procedures. In Fig. 5, curve (a) shows the shift as a function of temperature T_i, where, T_i is the temperature where the field cooling began until the sample was cooled down to 10 K (prior to this cooling the sample was cooled in a zero-field from 300 K to T_i). Curve (b) shows the shift induced when the sample was field cooled from 300 K to a temperature T_f, below which the sample was cooled in zero field to 10 K and shift measured. In order to keep the same reference temperature for all the data points the shift was always measured at 10 K. A sharp drop in the shift between 150 and 200 K implies a loss of exchange. In curve (a) of Fig. 5, even when the sample is cooled only from 30 to 10 K, a major portion of the shift (~95%) still remains, which implies the presence of Co_3O_4 in the sample in addition to CoO, whose effect always remains in the case of curve (a), unlike in curve (b).
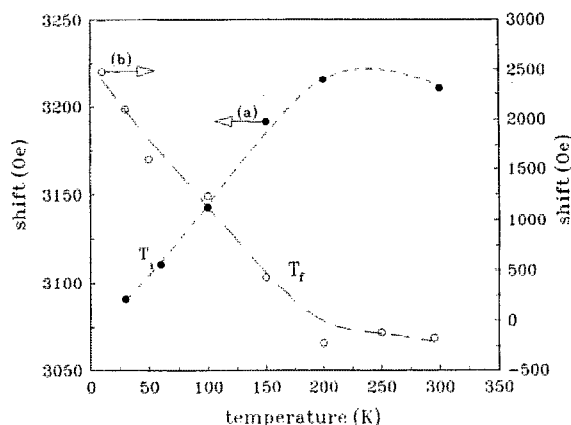

FIG. 5. Shift measured at 10 K. In curve (a) ● marks the temperature where field cooling began and in curve (b) ○ marks the temperature where the field cooling stopped, after being field cooled from 300 K.

CONCLUSIONS

The hysteresis loop shift, which is proportional to the interface exchange anisotropy, is found to depend on particle size and the extent of surface passivation, which is consistent with the exchange anisotropy model. The behavior of the loop shift with decreasing particle size resembles that of the Ni-Mn and related alloys. The change in shift and remanence with temperature are very similar to those observed in Ni-Mn alloys though they might have different origins. A comparable volume ratio of antiferro to ferro phases and a high density of interfaces are required to produce a large exchange interaction.

The presence of large unidirectional exchange anisotropy confirmed the core-shell structure in Co-Co-oxide particles. The large coercivities (about 6 kOe)[8] observed in these passivated Co particles at cryogenic temperatures can be explained in part by the existence of this interface exchange anisotropy.

ACKNOWLEDGMENT

[1] W. H. Meiklejohn and C. P. Bean, Phys. Rev. **105**, 904 (1957).
[2] W. H. Meiklejohn, J. Appl. Phys. **33**, 1328 (1962).
[3] J. S. Kouvel and C. D. Graham, Jr., J. Phys. Chem. Solids **11**, 220 (1959).
[4] J. S. Kouvel, J. Appl. Phys. **31**, 142S, (1960).
[5] J. S. Kouvel, J. Phys. Chem. Solids **21**, 57 (1961).
[6] F. J. Darnell, J. Appl. Phys. **32**, 186S (1961).
[7] J. S. Kouvel, J. Phys. Chem. Solids **24**, 795 (1963).
[8] S. Gangopadhyay, G. C. Hadjipanayis, C. M. Sorensen, and K. J. Klabunde, IEEE Trans. Magn. **28**, 3174 (1992).
[9] C. G. Granqvist and R. A. Buhrman, J. Appl. Phys. **47**, 2200 (1976).
[10] S. Gangopadhyay, G. C. Hadjipanayis, B. Dale, C. M. Sorensen, K. J. Klabunde, V. Papaefthymiou, and A. Kostikas, Phys. Rev. B **45**, 9778 (1992).
[11] A. P. Malozemoff, Phys. Rev. B **35**, 3679 (1987).
[12] D. Mauri, H. C. Siegamnn, P. S. Bagus, and E. Kay, J. Appl. Phys. **62**, 3047 (1987).