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Magnetic properties of cluster-beam-synthesized cobalt: Noble-metal films

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A cluster-beam deposition technique has been used to produce magnetic clusters embedded in a nonmagnetic matrix. We report here on films with cobalt clusters of average diameter of 5.5 nm embedded both in Cu and Ag. Volumetric concentrations of Co ranged from 10% to 50%. Magnetization and low temperature hysteresis loops, both field cooled (FC) and zero-field cooled (ZFC), have been measured between 4.2 and 300 K. The FC and ZFC magnetization bifurcate at or above room temperature with the clusters having a nonzero remanence at room temperature. Low temperature hysteresis loops exhibit a two-phase nature with one phase displaying exchange bias upon field cooling, suggesting the presence of an oxide phase. Conditions under which the oxide is present have been studied. © *2000 American Institute of Physics.* [S0021-8979(00)47408-6]

Nanoscale magnetic clusters embedded in a nonmagnetic matrix may have interesting intrinsic properties as well as high potential for applications such as high-density recording media or sensors based on their magnetoresistive properties. Such systems also offer the potential of a highly tailorable system in which to investigate magnetic interactions and phenomena. By systematically varying cluster concentrations while keeping their size constant, one can investigate intercluster interactions. Alternatively, a low concentration of varying sizes of clusters allows one to investigate the magnetic properties of the individual clusters. Thus, these systems have been ideal for use in the study of individual cluster magnetism[1–6] as well as collective dynamics and random anisotropy effects.[7–11] For certain combinations of cluster size and concentration, the system will change from behaving as a group of individual particles, or as a superparamagnetic system, to more a collective behavior, which might involve spin–glass or random–anisotropy transitions. Previous studies have investigated the similarities and differences of superparamagnetic clusters compared to a spin–glass system.[12,13] However, these studies were not able to vary independently the cluster concentration and diameter. This limitation, resulting from the sample-preparation method, makes it difficult to measure the concentration/cluster volume regime where such a system goes from being superparamagnetic clusters to a more collective or interactive system. We present here magnetic properties of cobalt clusters assembled by a method that is not subject to this limitation.

Samples were prepared using a cluster-beam-deposition system.[14–17] This technique uses a high-pressure (0.1–10 Torr) magnetron sputtering source with a gas-aggregation tube at liquid-nitrogen temperatures to create a cluster beam. These clusters are then softly landed on a substrate held at room temperature. Simultaneously, conventional magnetron sputtering is used to codeposit the nonmagnetic matrix on the substrate. Soft landing has the advantage that the clusters retain their spherical shape. For larger diameter clusters, this soft landing also tends to lead to a shadowing effect of the sputtered matrix. Since the matrix is not sputtered normal to the substrate, large clusters that protrude from the surface will create shadow regions where the deposition rate of the matrix will be lower. Thus, these films tend to become porous as the cluster size and concentration increases.[18] This method has been used to create several different systems including Co clusters in Ag, Au, Cu, and SiO_2. Cluster sizes can range in diameter from about 2 to 6 nm and in concentrations from 10% to 50%. The size of clusters follows a lognormal function with a very narrow size distribution measured by time-of-flight (TOF) and transmission electron microscopy (TEM).[16] We report here on samples with a cluster diameter of 5.5 nm in concentrations of 10%, 30%, and 50% both in Ag and Cu. We also discuss some preliminary results from cobalt clusters in SiO_2. These films were deposited on Si ⟨100⟩ wafers with a thickness of 350 Å and a 30 Å cover layer of matrix (250 Å for the SiO_2 case). These samples were then stored in air for several months before magnetic measurements were performed.

We have measured, with a superconducting quantum interference device (SQUID) magnetometer, the field-cooled (FC) and zero-field cooled (ZFC) low-temperature hysteresis loops as well as the magnetization as a function of temperature. For 30% and 50% concentrations in both Cu and Ag

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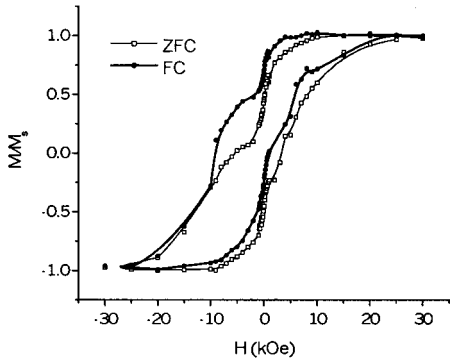

FIG. 1. Hysteresis loops of 5.5 nm Co clusters in Ag at 10 K. The cluster concentration is 50%. Both loops display a two-phase nature, but the FC loop also displays exchange bias.

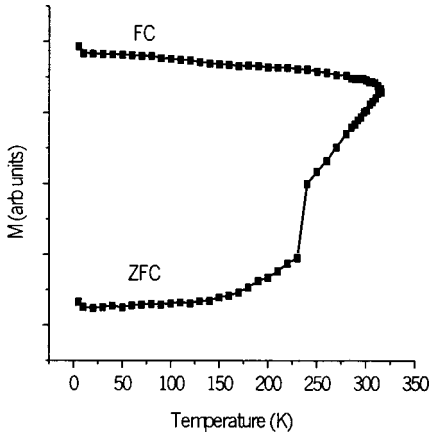

FIG. 3. FC and ZFC M vs T curves. Films were 5.5 nm Co clusters in Ag at 50%. The applied field was 50 Oe.

hysteresis loops at low temperature display a two-magnetic-phase nature (see Fig. 1). Fitting of both the FC and ZFC cases is achieved by a superposition of loops associated with two different magnetic subsystems. One subsystem is magnetically soft and has a coercivity of a few hundred Oersted with a narrow switching field distribution ($\approx$1 kOe). The other subsystem is magnetically harder having a coercivity of approximately 8 kOe with a larger switching field distribution ($\approx$10 kOe). Upon field cooling, this hard subsystem exhibits an exchange bias and shifts of up to 6 kOe depending upon the temperature and field cooling conditions. As seen in Fig. 2, by combining the magnetically ''soft'' subsystem loop with a loop corresponding to the magnetically ''hard'' subsystem in a 20:80 ratio by magnetization, we have arrived at a near match to the observed loops. The nature of the hard subsystem is consistent with a CoO phase magnetically coupled to some portion of the Co clusters. Co–CoO systems have been shown to have an enhancement to the coercivity of several kOe from that of Co and can display an exchange bias of up to 9.5 kOe[19] upon field cooling.

For the ZFC magnetization, the films were cooled to 5 K in the absence of an applied field. A 50 Oe field was then applied and magnetization was measured as the sample was heated to 310 K. The FC magnetization was then obtained by cooling the film in the 50 Oe field. For these 5.5-nm-diam clusters, the ZFC and FC magnetization bifurcate at or above room temperature for all three concentrations. At room temperature, the films have a nonzero remanence ($M_r/M_s = 0.27$) and exhibit hysteresis with $H_c = 150$ Oe. Thus, even for concentrations of 10%, interactions between clusters dominate over the superparamagnetic nature of the individual cluster as the superparamagnetic blocking temperature of these clusters is below room temperature. Additionally, for concentrations of 30% and 50%, we see a discontinuity in the ZFC magnetization between 230 and 240 K (see Fig. 3). This jump is not present in samples that do not exhibit the two-phase nature. This suggests that the jump is due to the oxide. As neither the Neél temperature of bulk CoO, ~290 K, nor that of Co_3O_4, ~40 K, is near this transition, it may be possible that the oxide is a disordered compound which undergoes a phase transition between 230 and 240 K. Another scenario is that finite-size effects reduce the Neél temperature of CoO[20] or the oxide becomes superparamagnetic at this temperature.[21] If either of these situations were true, then such a transition temperature would indicate that a large fraction of the cluster volume is oxidized. These mostly oxidized clusters would then be magnetically coupled to non-oxidized clusters. Evidence for such CoO clusters is seen in plan-view TEM as seen in Fig. 4. High resolution electron diffraction indicates some clusters have a face-centered-cubic (fcc) structure with a lattice parameter of 4.22 Å. This parameter is much closer to the 4.261 Å of CoO than it is to the 3.542 Å of pure cobalt.

In order to further investigate the apparent oxidation phenomenon, Co was deposited in a SiO_2 matrix with a 250 Å cover layer of SiO_2. These clusters, although the same diameter, do not display any exchange bias when field cooled to 5 K in 50% or 30% concentrations. Thus it is possible to create clusters that are not oxidized. This suggests the oxygen in the Co:Cu and Co:Ag films must have entered the samples after deposition. The simplest explanation is that after the samples were removed from the deposition chamber, air slowly diffused through the samples which, as mentioned above, are somewhat porous. Work is in progress to produce two sets of similar samples with one set

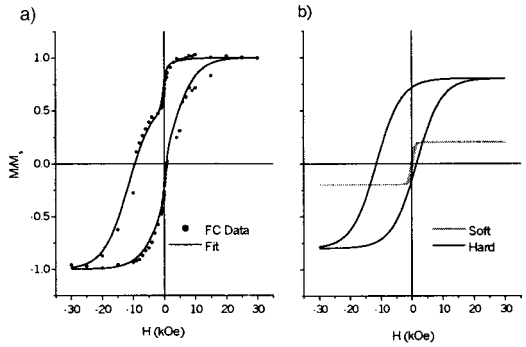

FIG. 2. (a) Fit of FC loop at 10 K. The coercivity of the hard subsystem is 6.5 kOe with an exchange bias of 5 kOe and a switching distribution of 8 kOe. The soft subsystem has a coercivity of 300 Oe and a switching distribution of 1 kOe. The two loops from the individual subsystems are shown in (b).

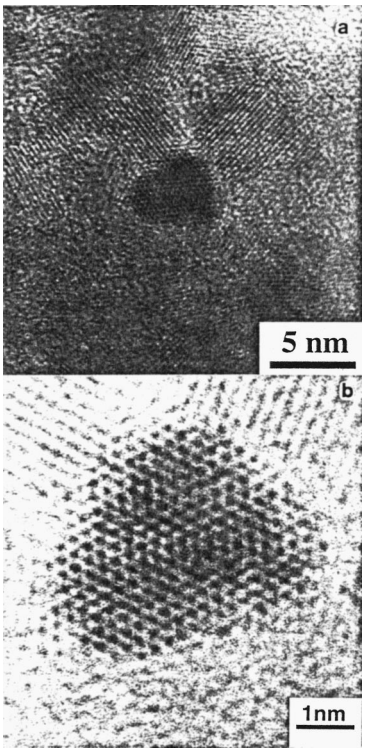

FIG. 4. Plan view TEM of 50% Co in Cu. Grain size is approximately 5.5 nm.

protected from oxidation by a thicker coverlayer. This study should help us separate phenomena associated with the cluster/matrix system from that of the oxide phase.

In summary, we have measured the magnetic properties of Co clusters in a nonmagnetic matrix. The clusters were deposited by a method that allows independent control of the size and concentration of the clusters. Samples with larger concentrations displayed evidence of exchange bias that can be associated with a Co–O magnetic subsystem. This oxide phase was present in both the Cu and Ag matrices, but not present in the SiO_2 matrix with a much thicker coverlayer. Further studies are underway on the fabrication and study of Co and other magnetic nanoscale clusters in various magnetic and nonmagnetic matrices.

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