PHYSICAL REVIEW B **69**, 172402 (2004)

Magnetic response of dilute cobalt nanoparticles in an organic matrix: The effects of aging and interface chemistry

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(Received 10 February 2004; published 5 May 2004)

We report studies of the magnetic response of dilute frozen solutions of nanocrystalline Co particles grown in inverse micelles. Crystalline nanoclusters which initially exhibit only a small fraction of the bulk saturation moment restructure in solution without any change in cluster size or blocking temperature over a period of ~30–60 days, finally yielding a moment/atom which exceeds that of bulk Co. The saturation magnetism maintains its enhanced value for temperatures up to the melting point of the solvent matrix, but is strongly dependent on surface active additives and molecular oxygen.

DOI: 10.1103/PhysRevB.69.172402 PACS number(s): 75.75.+a, 36.40.Cg

The magnetic response of ferromagnetic clusters is known to be sensitive to modifications in the crystal symmetry, atomic coordination number, and the interatomic distance. Experiments on free beams of mass selected Co, Fe, and Ni clusters have demonstrated a significant increase in magnetic moment with decreasing size,[1,2] as well as evidence for structural isomers with significantly different moments. These isomers were found in the size range of $N=55-66$ atoms which is close to that expected for a stable cluster with three closed atomic shells and cubicosohedral symmetry. Two clusters with the same number of atoms but a different packing will likely have very different magnetic moments.

Unlike free clusters in beams with bare atomic surfaces, solution synthesized clusters can undergo collisions between clusters, and facile diffusion of atoms on the surface may occur with time. The chemical structure of the surfactant may affect its binding location and thus force a reconstruction of the surface with age. This could either enhance or reduce the magnetic response.

A suggestion of a cluster structural change which could affect the magnetic response of clusters grown in solution was first mentioned in the work of Griffith, O'Horo, and Smith where they noted that 6 nm Fe clusters allowed to age under Ar for ~1 yr exhibited changes in the selected area diffraction (SAD) pattern which they interpreted as a change from a partially disordered structure to an α-Fe bcc lattice with an unknown second phase.[3] Unfortunately, magnetic response measurements for the aged clusters were not reported but the disordered structure had only approximately 30% of the bulk magnetization. Their systems were stabilized by large polymers at the cluster surface which they suggested might account for the initially non-equilibrium disordered structure they observed.

A number of reports have appeared in the literature describing the magnetic behavior of nanosize clusters formed using colloidal chemistry methods which require a surfactant at the cluster surface to control the cluster size and ensure complete dispersion of the clusters. In the case of Co nanoclusters the moment/atom was either reduced,[4–6] comparable,[7] or enhanced[8–10] relative to the known bulk value of 1.72 μ_B/atom for hcp Co. TEM sometimes indicates an oxide shell on the surface of the clusters which could account for the reduced moments,[5] and in at least one case it was known that more than one magnetic phase of Co was present at the surface whose moment was extraordinarily large, 7.5 μ_B/atom.[11] Generally, enhanced moments were attributed to larger moments for surface Co atoms due to unquenched orbital angular momentum. Since each of these experiments used chemically different surfactants the nature and extent of the electron donating or withdrawing propensity of the surfactant may explain the diverse results. In this letter we investigate this hypothesis by the addition of surfactants to a Co nanocluster sample having the majority of its atoms at surface sites.

We report our observations of a large increase with time in the magnetic saturation or moment/atom in dilute solutions of Co nanoclusters when allowed to spontaneously anneal under Ar at room T in a hydrocarbon solvent. These clusters are small, with diameters 1.8 ± 0.2 nm and are stabilized against aggregation using alkylated polyether surfactants. Our experiments show that clusters are superparamagnetic for all temperatures $10<T<200$ K which exceed the observed blocking temperature, $T_B\sim7.5$ K (determined by the magnetism peak in warming data for a dilute sample field after zero-field cooling.

For the small Co clusters described in this work the majority of atoms (~76% for cubicosohedral symmetry), occupy surface sites, interacting with the surfactant and can diffuse easily at ambient temperature, causing changes in surface structure which, with age, increase the magnetic response dramatically, as we shall show.

These Co nanoparticles were formed by the reduction of $CoCl_2$ in decane using $LiAlH_4$. Since ionic salts like $CoCl_2$ are insoluble in oils we add a nonionic polyether ligand which forms inverse micelles in oil and dissolves the ionic salt $CoCl_2$, forming a transparent blue solution. Due to the strong oxygen and water sensitivity of metallic Co nanoparticles, we employ an inert gas glove box and an anerobic inverse micelle process to synthesize and handle the Co clusters.[12,13] Chemical interactions between the surface Co atoms and the surfactant prevent cluster aggregation with time, though each ether/Co interaction is weak allowing facile displacement by more strongly binding ligands after the synthesis—an important aspect of this study.

Figure 1 shows a high-resolution transmission electron microscopy (HRTEM) image of the particles. The cross-

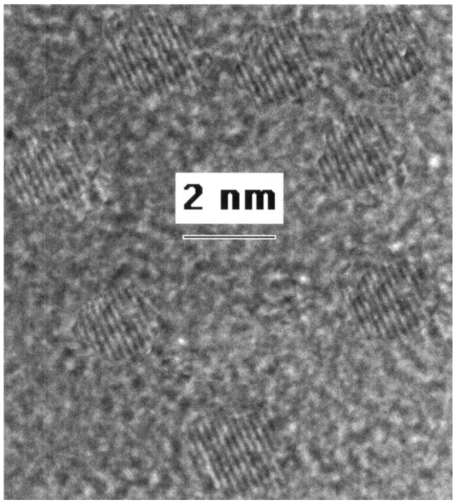

FIG. 1. High resolution (HRTEM) of showing an average size of $D \sim 1.8$ nm, and an interatomic spacing of ~2.0 Å.

sectional diameter is 1.8–1.9 nm with a measurement uncertainty of one lattice plane (~0.2 nm). A high-resolution size-exclusion absorbance chromatogram of the particles stabilized with hexadecylamine showed a single elution peak at $t = 8.0$ min which corresponds to a core size of 1.7–1.8 nm.[12] This elution peak had a Gaussian profile whose temporal width corresponds to a spread in size of, at most, ±0.2 nm, consistent with the HRTEM.

Various structures have been reported for Co nanoclusters, predominantly a face-centered-cubic phase, similar to bulk β-Co, with numerous stacking faults.[4,5,11,14,15] Other studies observed a complex cubic phase with a large unit cell termed ε-Co,[5] a hexagonal-close-packed structure, similar to bulk α-Co with stacking faults,[5,16,17] a body-centered cubic core with an hcp shell,[9] and a structure with polytetrahedral packing.[18] It is clear that the atomic arrangement is very sensitive to synthetic protocol, especially the surfactant used to passivate and stabilize the nanocluster surface. Never the less, the saturation magnetization in bulk α-Co and β-Co differ by less than 2%.[19] The lattice plane spacing of 2.0 Å in Fig. 1 is close to that observed in the (100) direction of hcp Co, 2.05 Å, but the 3D structure of our clusters is unknown. We observe subtle atomic restructuring of the cluster surface with age which strongly enhances the magnetic moment/atom of our clusters.

The magnetic response of a very dilute solution, ~0.05 wt. %, was studied using a commercial SQUID magnetometer (Quantum Design MPMS-7) calibrated with a Pd reference. For these measurements 200 μl of the sample was transferred using a digital pipette to a tared, 5 mm diameter, 6 in. length quartz NMR tube (Wilmad glass) and weighed. After sealing the tube with a silicone rubber cap, the net weight of our dilute Co sample in oil was measured in the glove box allowing accurate and reproducible values of the net weight of Co from the known molarity of the solution. The tube was transferred via interlock to our magnetometer and the solvent frozen.

A small portion of the sample was diluted ten fold and its concentration confirmed by x-ray fluorescence (XRF) using the Co $K\alpha$ line and compared to NBS traceable Co standards in xylene, so its concentration is known to ±3%. Our measurements are all obtained at high dilution of the Co nanocrystals in the decane solvent ensuring non-interacting individual superparamagnetic particles which follow the assumptions of the Langevin theory of superparamagnetism.

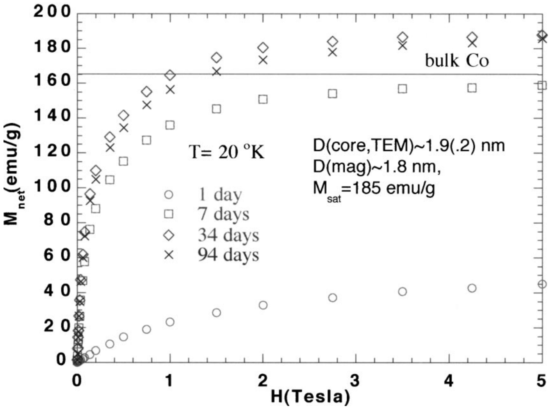

FIG. 2. Magnetic response, M_{net} of Co, $D = 1.8$ nm vs external applied field, and H as a function of sample age in decane. The solid line indicates the saturation magnetization of bulk HCP Co.

Due to the extreme dilution of the samples and the desire to have the magnetic signal approximate a point dipole, only about 0.12 mg of Co $(0.01M)$ is present in our sample, thus requiring a subtraction of the negative diamagnetic background from the solvent and quartz tube. This background corresponds to 1.26×10^{-7} emu/Oe at each applied field, H. The data shown reflect this background subtraction, which is only significant at high fields causing the M vs H data to have a negative slope.

The $D = 1.8$ nm dispersed Co sample in decane was zero-field cooled to 5 K and then heated in the presence of a small, $H = 10$ Oe field to examine the blocking behavior. The samples only show evidence for blocking and hysteresis in the magnetic response below $T = 10$ K. To preserve a random orientation of the Co clusters, we are limited at higher T by the melting of the solvent, typically decane. The temperature, T_B, where the cluster spin reorientation time approached the measurement time of 1 min and the sample magnetization during warming reached a maximum was around 7.5 K which is the lowest reported value in the literature. In a previous study of polymer-stabilized Co clusters, a value of $T_B = 9$ and 13.5 K were reported for $D = 1.5$ and $D = 2.0$ nm clusters respectively, which suggests these clusters were actually larger than in the present study.[10]

Magnetization data from freshly synthesized $D = 1.8$ nm, Co nanoclusters are shown by open circles in Fig. 2 and have low magnetic response, only about ~20% of the bulk. Upon annealing at ambient temperatures under Ar in a dilute solutions of decane, we observed an increase in magnetic saturation from only ~44 emu/g or 0.47 μ_B/atom after one day to 187 emu/g or 1.98 μ_B/atom after 30 days (values for bulk hcp Co are 161 emu/g or 1.71 μ_B/atom). During this process there is no significant change in T_B, which depends on the energy barrier for spin reorientation, or the cross-sectional size as observed in HRTEM. Thus, we suggest this large

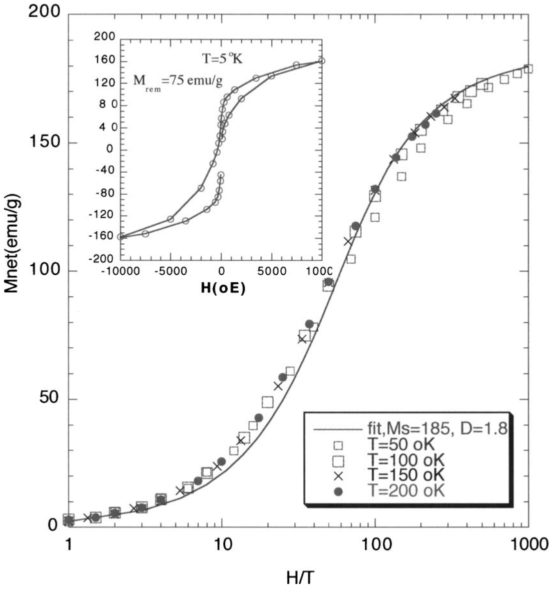

FIG. 3. Magnetic response data from a $D=1.8$ nm dilute, frozen solution of Co clusters for temperatures well above the blocking T closely follow the Langevin prediction (solid curve). The inset shows the low field data obtained at $T=5$ K, slightly below the blocking $T_B=7.5$ K.

increase in magnetic response is due to diffusion and restructuring of surface Co atoms to a more energetically favorable and more strongly magnetic cluster. After this initial period, no further changes in magnetic response occur as shown in Fig. 2.

The time required to achieve a full magnetization with room T annealing is very dependent on the solvent and reducing agent. The former affects the strength of the interaction between the nonionic surfactant and the Co surface while the latter appears to change the chemical properties of this surface and the strength of chemical interaction between nonionic surfactants and the Co cluster surface. Despite these complexities, we observed increases in magnetic response with age in Co samples of similar size prepared in alkanes such as hexane, octane, and hexadecane.

The observed increase in the magnetic response with age is likely due to changes in the surface morphology rather than a change in cluster mass since the magnetic volume (number of spins/cluster) for the all the data shown in Figs. 2–4 shows blocking at ~7.5 K independent of age. Size-exclusion liquid chromatography and HRTEM on the aged sample confirms no cluster size change occurs as a result of aging.

If a portion of the sample is placed in a sealed tube in a block heater set to a mild temperature of ~60 °C it is possible to accelerate the Co surface changes and reach the ultimate magnetic response shown in Fig. 2 in a few days.

Figure 3 shows that these clusters, once fully annealed, follow Langevin behavior expected of dilute independent superparamagnets when fit with a spherical magnetic size of $D=1.8\pm0.1$ nm, a value in close agreement with the TEM cross section of 1.8 ± 0.2 nm, and a saturated magnetic value of $M_S=185$ emu/g. Closer to the blocking T a small systematic deviation from this simple behavior was found, similar to that observed for much more concentrated $D=1.6$ nm Co nanoclusters in a polymer by Osuna *et al.*[8,10] However, in the present case our Co concentration was only ~0.06 wt. % compared to the 12 wt. % sample used in these previous studies which found significant deviations from Langevin behavior at high H/T values. Since the mean interparticle spacing is only ~3.4 nm for a 1.5–2 nm particle at this concentration, the previous observed deviations from ideal Langevin behavior which were attributed to structural anisotropy may have been due to dipole-dipole interactions or cluster aggregation, both of which would lead to a higher value of T_B compared to the present work.

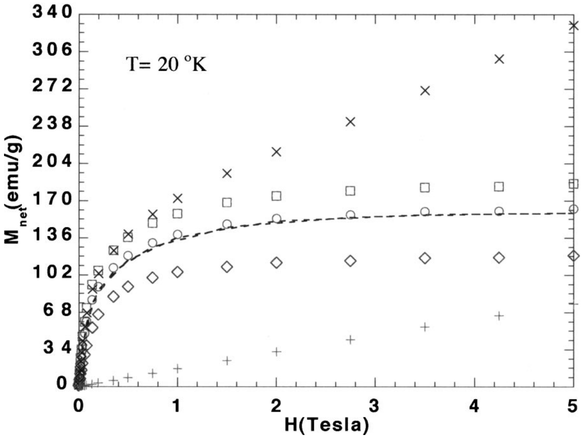

FIG. 4. A $D=1.8$ nm Co nanocluster dispersion in decane is exposed to equilmolar amounts of surfactants with chemically distinct heteroatomic head groups. Crosses are hexadecylamine, squares are oleic acid, circles are trioctyl phosphine, diamonds are dedecanethiol, and crosses are oxygen exposure for several days. The dashed curve is the parent sample stabilized with a nonionic surfactant.

Only the lowest T investigated, $T=5$ K was hysteresis observed in the magnetic response as shown in the inset to Fig. 3. We estimated a remnant magnetization of ~75 emu/g and a coercive field of ~250 Oe at this T, which is, unfortunately, very close to T_B.

The aging effect shown in Fig. 2 reflects the large number of nonequilibrium surface positions for Co clusters of such small dimensions and their influence on the magnetic response. We expected that any chemical change to these surface atoms would have a strong influence on the magnetic response.

To investigate this issue we added an equilmolar quantity ($0.01M$) of each of the surfactants indicated in Fig. 4 to a $D=1.8$ nm Co solution after 7 days of annealing (dashed curve in Fig. 4). At this time M_S was equal to that found in bulk hcp Co. As anticipated we observed that displacement of the nonionic polyether surfactant by other types of surfactants alters the magnetic response in most instances.

We chose surfactants which are commonly used to sterically stabilize larger Co clusters grown by high T thermal decomposition of organometallic precursors since we wondered if their interaction with the surface could explain the low values of M_S observed with these surfactants.[5] As shown in Fig. 4, oxidation of the clusters by exposure to air drastically changes both the shape of the magnetic response curve and its high field response. Addition of tri-octyl phosphine had no effect on the magnetic response, indicating that it may not bind at any surface sites of Co clusters. The other surfactants have little effect on the low field magnetic response but induce major changes at high field.

The largest changes occur in the case of dodecanethiol and hexadecylamine, both of which are known to bind quite strongly to a variety of metals. The alkane thiol lowers the magnetic response from ~170 emu/g to ~110 emu/g at $H = 5$ T. One can rationalize this observation by assuming that electron donation by the lone pair of electrons on the sulfur into the empty *d* orbitals of the Co atoms at the surface lowers the net spin of these atoms. However, one would expect the same decrease in net spin of the surface Co atoms to occur in the case of the hexadecylamine. Instead, we observe a strongly enhanced moment with a nearly linear high-field response and a value of over 300 emu/g at our highest field, $H = 5$ T. However, at low fields, the shape of the magnetization curve closely follows that of the other samples with the other surfactants.

Though it has been demonstrated previously that binding of molecules like CO to $D = 1.6$ Co clusters in a polymer can significantly reduce M_S to a value of 55 emu/g,[8] the behavior shown with hexadecylamine is unprecedented and very puzzling. Simple oxidation of the clusters to superparamagnetic Co(II) yields a very different behavior as we verified by magnetic measurements of the blue, paramagnetic Co(II) precursor solutions which exhibit only ~100 emu/g at 5 T at this concentration and temperature. In fact, the hexadecylamine data can be fit to a two-component sample containing Co clusters (dominant at low fields) and a paramagnetic species with a moment of a few μB. This behavior is reminiscent of the heterogeneous core-shell data reported by Chen *et al.*[11] However, in that work the shell was attributed to the formation of cobalt boride at the surface due to the use of $NaBH_4$ as the reductant.

In conclusion, we have demonstrated that $D = 1.8$ nm Co clusters in frozen solutions of linear alkanes can exhibit magnetic enhancements of ~10% compared to bulk Co. Such enhancements were previously observed in free beams of clusters of similar numbers of atoms.[2] However, our clusters initially have low magnetic response and require room T annealing for many days before exhibiting their ultimate magnetic properties, which are then stable for periods exceeding several years if stored under Ar. We attributed the observed improvement in magnetic response to facile surface diffusion of atoms and reconstruction of the surface. No change in the blocking T was observed during these changes in high field magnetic response, consistent with measurements of an invariant size by TEM.

Exposure of the surface of these clusters to various commonly used strongly binding ligands such as alkyl amines and thiols revealed the important role that the surfactant electron donation plays in the magnetic response. Most surfactants investigated had minor effects on the low field response and either left invariant or lowered the high field response. An exception was the strange linear response of hexadecylamine which contrasts with all the other electron donating surfactants we investigated.

The strong magnetic response of these Co clusters can be affected negatively by many factors the most obvious being oxidation of the surface. Perhaps our most surprising observation was that an attempt to deposit more Co atoms onto the clusters by chemical reduction of an equal number of Co(II) ions in inverse micelles results in a dramatic loss of over 70% of the high field magnetic response. This is a much larger decrease than we observe when simply adding Co(II) ions to the solution. This deposition of slightly less than a monolayer destroys the strong magnetic response of the $D = 1.8$ nm clusters nearly as effectively as oxidation. However, about 75% of the original, 185 emu/g saturated magnetic response can be restored by simple thermal annealing in a sealed vial under Ar at a modest $T = 60\,^\circ\mathrm{C}$ for three days, indicating a metastable, low magnetic surface was created that can reconstruct over time to a more stable, magnetically responsive cluster. In future work, we intend to investigate slower atomic deposition by reduction of Co(II) from solution to synthesize larger clusters with magnetic response comparable to bulk hcpCo.

This work was supported by the Division of Materials Science and Engineering, Office of Science, US Department of Energy under Contract No. DE-AC04-AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the US Department of Energy.

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