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Magnetization of cobalt nanodiscs

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Abstract

We have studied the magnetization and AC susceptibility of a dilute colloidal dispersion of ε-Co nanodiscs. The temperature dependence of the magnetization implies that the nanodisc moments become largely static below a blocking temperature which exceeds room temperature. The related anisotropy energy is significantly larger than the magnetocrystalline anisotropy for bulk ε-Co, which may result either from surface modifications to the crystalline anisotropy, or perhaps from shape anisotropy. The saturation moment is found to be temperature independent, over a wide range of temperatures and also close to the blocking temperature, although the field at which saturation occurs varies considerably with temperature. A coercive field of 1700 Oe is found at low temperature, indicating that magnetization reversal involves the coordinated rotation of the moments in individual nanodiscs. Aging effects are observed in the AC susceptibility, implying that the spatial coherence of the room temperature dispersions increases over time, leading to static short-range order.

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Keywords: Cobalt nanodiscs; Magnetization reversal; Magnetic anisotropy

Much interest in assemblies of magnetic nanoparticles is driven by their novel short-range ordering properties, and by their associated dynamics. So far most work has focussed on suspensions or composites of nearly spherical nanoparticles composed of materials which are ferromagnetic in the bulk [1,2]. The nanoparticle diameters are typically in the range 2–20 nm, which ensures that there is a single magnetic domain in each nanoparticle. The dynamics of the nanoparticle moment reflect a free energy landscape which is dominated by two states describing opposite nanoparticle magnetizations, separated by an energy barrier which may be varied by applied magnetic field. The effects of particle size [3–5], polydispersivity [6,7], and separation [3,8,9]

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on the overall magnetic properties of these nanoparticle systems have received extensive experimental study. Consequently, it is believed that the nanoparticle anisotropy, which can originate from any or all of the crystal field, the surface, or the shape of the particle, largely determines the magnitude of energy barrier, while interparticle interactions generally provide a secondary modulation or substructure to the free energy landscape.

Relatively little attention has been focussed on the role of nanoparticle shape in the magnetization process. Nonetheless, this is an issue of considerable technological importance, since coercivity and thermal stability of the magnetization are key considerations for magnetic recording applications. Experimental studies on arrays of magnetic nanowires, prepared by the electro-deposition of ferromagnetic metals in porous host materials indicate that substantial enhancement of coercivity can be realized in the cylindrical geometry [10–14]. However, the nanowires in these arrays are closely spaced, and must be presumed to be strongly interacting. By analogy to the large body of work on spherical magnetic nanoparticles, what is needed instead is a dilute and monodisperse suspension of anisotropic particles, where the intrinsic properties of the individual nanoparticles can be isolated. This study has only recently become possible, due to the discovery of a size-controlled synthesis of colloidal dispersions of cobalt nanodiscs, and related structures [15–18]. We report here on the magnetic properties of a dilute suspension of cobalt (Co) nanodiscs, which will be compared to results on the more familiar dispersions of spherical nanoparticles, in order to highlight the role of shape anisotropy. As we will show, the magnetic behavior of these nanodiscs is similar in several ways to that of magnetic nanowire arrays.

Co nanodiscs were prepared by injecting the molecular precursor $Co_2(CO)_8$ dissolved in o-dichlorobenzene (DCB) into a refluxing bath of trioctylphosphine oxide (TOPO), hexadecylamine and oleic acid dissolved in DCB [15–18]. Subsequently, the oleic acid coated nanodiscs were suspended in DCB, with a nominal separation of ~80 nm, determined by measuring the volume concentration of Co using X-ray fluorescence (XRF). A TEM micrograph of particles from this suspension is shown in Fig. 1. The smallest elements are Co nanodiscs, which are cylinders of approximate dimensions of 25 nm diameter × 4 nm height, not including the surfactant coating. The individual nanodiscs have stacked into long rods, along the cylindrical axis of the individual nanodiscs (Fig. 1), as has previously been observed [15]. Electron diffraction measurements indicate that the nanodiscs form in the ε-Co structure [17].

We performed dynamical light scattering measurements on the newly synthesized suspensions of nanodiscs, and determined that the radius of gyration of these rods is approximately 100 nm. One interpretation of these data is that the average length of rod formed by these nanodiscs is ~350 nm. This is similar to the average rod length deduced from the TEM experiments, so we conclude that the diffusive motion of the stacked discs is essentially unconstrained, probably because we used very dilute suspensions for this measurement. This suggests that the stacks of nanoparticle discs are not highly entangled, and can be uniformly diluted, at least in freshly synthesized suspensions. We repeated the light scattering measurements after several months had elapsed, and found that the particles in the suspension were apparently larger and more structured than immediately after synthesis,

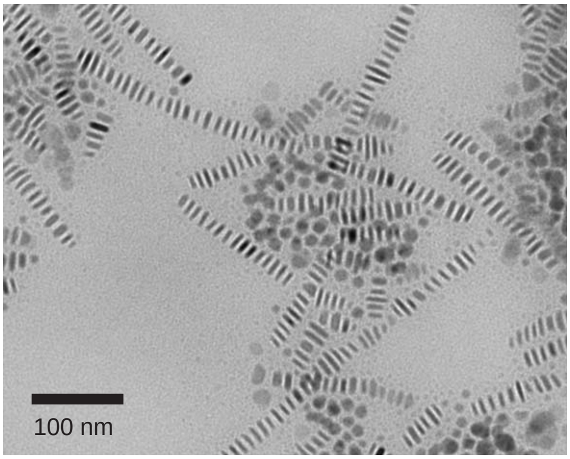

Fig. 1. Transmission electron microscope image of stacked Co nanodiscs.

suggesting that the stacks of nanodiscs had undergone some degree of agglomeration or entanglement. Magnetization and AC susceptibility measurements were carried out on both the as-synthesized and aged nanodisc suspensions using a Quantum Designs Magnetic Phenomena Measurement System (MPMS).

The temperature dependence of the magnetization is consistent with a scenario in which the nanodiscs are superparamagnetic above ~300 K, with the nanodisc moments becoming blocked or static at lower temperatures. The temperature dependences of the 100 Oe field-cooled (FC) and zero-field-cooled (ZFC) magnetizations are compared in Fig. 2. Although measurements were not carried out above the 250 K melting point of DCB, the FC and ZFC curves appear to converge near room temperature, providing a lower bound for the blocking temperature T_B of this system of 300 K. We note that there is no structure in the FC and ZFC $M(T)$ curves at low temperatures which might suggest either the presence of magnetic impurities or appreciable numbers of individual nanodiscs which are not included in the rodlike structures observed in the TEM experiments. Since the individual nanodiscs are well below the single domain limit for Co, we can estimate the effective anisotropy energy K of the Co nanodiscs using the relationship [19] $T_B = \Delta E/30k_B$, where the effective energy barrier $\Delta E = KV$. Taking the particle volume V to be $\pi r^2 H = 3.14 \times 10^{-25}\,\text{m}^3$, we find $K = 3.95 \times 10^5\,\text{J/m}^3$. This value is substantially larger than that determined for bulk ε-Co, $K = 1.5 \times 10^5\,\text{J/m}^3$ [20], suggesting that either the surface [21,22] or shape anisotropies [23] are more important than magnetocrystalline anisotropy in determining the energetics of these Co nanodiscs.

The field dependence of the magnetization suggests that the thermodynamic potential which separates the blocked states with the net nanoparticle moments parallel and antiparallel to the anisotropy directions is very steep, and that the internal rigidity of the two blocked states is consequently very high. The field dependences of the magnetization are presented in Fig. 3 for several temperatures in the blocked state. In each case, the magnetization approaches a saturation value M_S of ~900 emu/cm³ of Co, which is only 60% of the value for bulk HCP Co [27]. This result is surprising, as it has previously been shown [3] that the saturation magnetization is actually slightly enhanced in small, spherical Co particles, presumably by the reduced dimensionality of the surface moments. It is in principle possible that a substantial fraction of the nanodisc volume in our

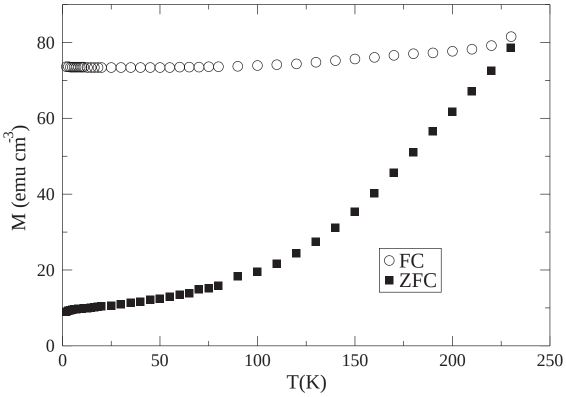

Fig. 2. The temperature dependences of the zero-field-cooled magnetization (filled squares) and the magnetization cooled in a field of 100 G (open circles).

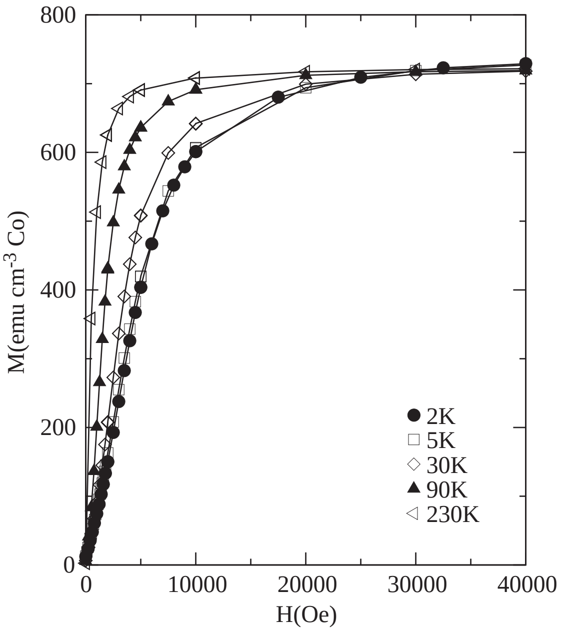

Fig. 3. The field dependence of the magnetization at several different temperatures in the blocked state.

experiment is magnetically inert, perhaps due to oxidation of the surface [24–26]. We think this explanation is somewhat unlikely, as it would indicate that the anisotropy of the nanodiscs mentioned above is a substantial underestimate, with the actual value approaching $6.6 \times 10^5\,\mathrm{J/m^3}$, more than four times larger than the magnetocrystalline anisotropy for bulk ε-Co.

It is quite remarkable that the saturation moment is virtually temperature independent for temperatures in the blocked state from 2 to 230 K, as previous measurements on spherical Co nanoparticles [21] found a steady increase in M_S with decreasing temperature. Since the conventional expectation is that reducing temperature reduces the admixture of the two magnetization states and leads to an overall larger magnetization, our results instead indicate that the corresponding minima in the thermodynamic potential must be exceptionally steep. This implies that excitations are only effective in changing the magnetization of the nanodisc assembly for temperatures very near and above the blocking temperature. This does not mean, however, that the development of the low-field magnetization of our nanodiscs is insensitive to temperature. As the temperature is reduced, the magnetization saturates above progressively higher fields, indicating that there are fewer configurations of the individual moments comprising the net nanoparticle moment possible at low temperature. We note that this is in clear contradiction to the law of approach to magnetization saturation, which predicts that saturation is more easily achieved at low temperatures, provided that the saturation moment is temperature independent as in Fig. 3.

The full magnetization loop at 2 K is shown in Fig. 4. As the sample was cooled in zero field, the initial zero-field magnetization is very small, and the system is induced into two states of opposite magnetization, with a frozen in coercive field H_C of ~1700 Oe at 2 K, far below the system blocking temperature.

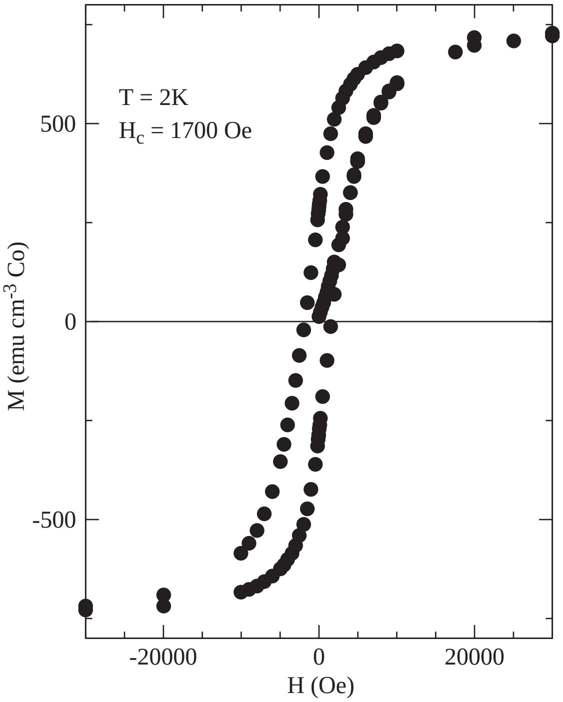

Fig. 4. A magnetization loop of our nanodisc assembly at 2 K, deep in the blocked state. The coercive field is 1700 Oe.

Two different scenarios for magnetization reversal may be considered in our system of stacked nanoparticles. In the first, the magnetization reversal occurs independently in the individual nanodisks, implying that the coercive field would be similar to that of other nanoparticles with similar anisotropies K. Alternatively, the magnetization reversal may involve the simultaneous and coherent rotation of the magnetizations in each of the nanodiscs in the stack. Our observed low-temperature value of 1700 Oe is far smaller than the low-temperature limit of $H_C = 2K/M_S = 5500\,\mathrm{Oe}$. At the same time, the 1700 Oe coercive field is significantly larger than the 1200 Oe found in spherical Co nanoparticles of similar size [21], as expected for the larger anisotropy of the nanodiscs. Finally, we note that the coercive field for our nanodisc system is much larger than the ~0.01 T which we extrapolate from reported values for Co nanowires with the diameter and length of individual nanodiscs, i.e. 25 nm × 4 nm [12,13].

Our magnetization data suggest that the magnetization reversal involves the cooperative and coherent rotation of the magnetizations in the entire stack of nanodiscs, over distances which approach the length of the nanodisc stack,

~350 nm. Indeed, our measured 1700 Oe coercive field compares favorably with the 2300 Oe found for a 350 nm, 2000 nm^3 Co nanowire [12,13]. Of course, the morphology of our sample suggests that interactions among neighboring stacks of nanodiscs are likely to be much weaker than those among neighboring magnetic nanowires, even considering that interactions may enhance the coercive field in the magnetic nanowire arrays. Alternatively, the activation volume for the magnetization reversal may not be identical to the average volume of the nanodisc stack, due to stacking defects or perhaps oxidation effects. Even considering these potential complications, we believe that the magnetic properties of our suspensions of Co nanodisc stacks are very similar to those of magnetic nanowires.

Finally, we measured the AC susceptibility in an oscillating field strength of 4 G, and for frequencies between 83 and 175 Hz. As indicated in Fig. 5, the real χ' and imaginary χ'' parts of the susceptibility of the as-synthesized nanodisc suspension are almost temperature independent, although a pronounced peak in χ'' is observed between 20 and 60 K, whose amplitude increases with increasing frequency. We suggest that this increased dissipation may result from residual interactions among the stacks of nanodiscs, leading to short-range magnetic order in this range of temperatures. The frequency dependence indicates that this order is largely associated with dynamical freezing, and not with long-range spatial correlations, consistent with the metastable and overall disordered character of this magnetic system. We repeated these measurements several months after the sample was synthesized, with very different results (Fig. 5). The short-range order peak had disappeared from χ'', and at the same time the real part of the low-temperature susceptibilty had been greatly enhanced. These observations indicate that short-range magnetic correlations evolve over time into stable and frozen magnetic order, with substantially extended spatial correlations. Apparently, the stacks of magnetic discs attract each other in room temperature suspensions, and under the action of these magnetic interactions form soft but extended magnetic solids.

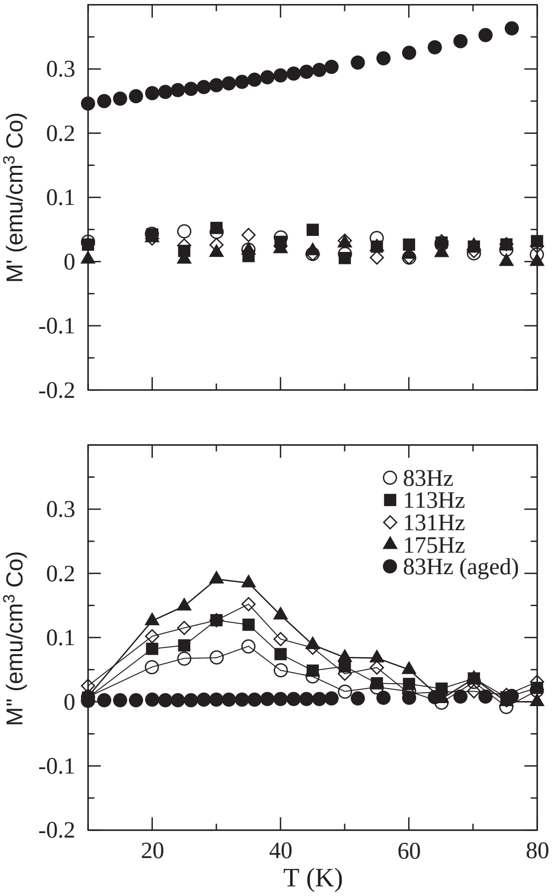

Fig. 5. The real (a) and imaginary (b) parts of the AC susceptibility of a newly synthesized suspension of Co nanodiscs in a field of 4 G, at different measuring frequencies. The solid circles are measurements at 83 Hz of the same sample after 2 months have elapsed.

In conclusion, our measurements on a dispersion of stacked ε-Co nanodiscs show that their magnetic properties are in qualitative agreement with the generic expectations of the Neel–Brown model. The blocking temperature for the nanoparticle moments is in excess of 300 K, implying an anisotropy which may be as large as four times the bulk value for ε-Co. We find that the saturation magnetization is unusually temperature independent, relative to what is expected for spherical particles of a similar anisotropy, suggesting that the free energy is an unusually strong function of the configuration variable for nanodiscs. Finally, we observe that the coercive field at low temperatures is comparable to that for a Co nanowire whose length is the stack length, not the length of the individual nanodiscs. We conclude that the magnetization reversal requires the coherent and simultaneous rotation of the magnetizations in each nanodisc in the stack.

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