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Self-stabilized magnetic colloids: Ultrafine Co particles in polymers

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Self-stabilized magnetic colloids consist of magnetic particles dispersed in an appropriate matrix. Fixing the particles in a stabilizing matrix has the advantage of preventing particle agglomeration, increasing resistance to oxidation, and allowing control over the interparticle spacing and particle size. We describe the chemical synthesis of cobalt nanoparticles in a polystyrene/triphenylphosphine polymer matrix. Depending on the synthesis parameters, magnetic properties of the as-synthesized nanocomposites range from superparamagnetic to ferromagnetic with coercivities on the order of 130 Oe. Solvent choice and polymer crosslinking significantly affect the magnetic properties. Annealing in vacuum produces coercivities of up to 600 Oe and remanence ratios of up to 0.4. Measurement of the isothermal remanence magnetization and dc demagnetization indicate the presence of both magnetizing and demagnetizing interactions, in contrast to particles synthesized without the polymer, which show no evidence for magnetizing interactions. The zero-field-cooled temperature-dependent magnetization displays a cusp, while the field-cooled magnetization increases monotonically below the cusp temperature. Glassy behavior is observed for temperatures below the cusp, although the mechanism producing this behavior is not yet understood. © *1996 American Institute of Physics.* [S0021-8979(96)01908-3]

Nanoscale particles have unique electrical, chemical, structural, and magnetic properties, with potential applications in information storage, color imaging, catalysis, bioprocessing, magnetic refrigeration, and ferrofluids.[1] Fabrication techniques for the production of ultrafine particles include: gas condensation,[2] inverse micelle synthesis,[3] arc techniques,[4] sputtering,[5,6] self-assembled phospholipids,[7] chemical reduction,[8–10] and microemulsion synthesis[11] among others. Studies of these systems are often hampered by two problems. First, the large ratio of surface-to-bulk atoms results in high reactivity. While desirable for catalysis, reaction with oxygen can adversely affect magnetic properties. Controlled passivation can deactivate the particle surface; however, this may form additional magnetic phases that complicate analysis. The second problem is the spontaneous production of macroscopic-sized agglomerates that lack the unique properties of nanoscale particles.

The fabrication of highly reactive particles by the reduction of metal halides was pioneered by Rieke and collaborators.[9] In this technique, a metal salt is reduced using a hydrocarbon or ethereal solvent in the presence of lithium and naphthalene. We have extended this technique to fabricate cobalt particles in a polymer matrix, which decreases agglomeration and improves oxidation resistance.

Self-stabilized colloids have been fabricated using other techniques, including ion exchange[1,12] and sputtering;[6] however, in most cases the particle size is small and cannot be conveniently varied. These systems tend to be superparamagnetic unless the metal volume concentration is above the percolation point. On the other end of the size scale, macroscopic composites of 10–100 μm transition metal[13] and ferrite[14] powders in polymers have been fabricated to study modifications of electrical and magnetic properties.

We have synthesized Co nanocomposites using a poly-styrene backbone and triphenylphospine sidechains. Samples have been synthesized using both a commercially available crosslinked polymer and a linear polymer. Different solvents were chosen to assist in the synthesis: solvent choice has been shown to affect particle size during standard syntheses[9] (i.e., without the polymeric matrix). The cobalt loading was determined to be 70% through chemical assaying. X-ray diffraction of the as-synthesized samples shows no evidence of crystalline cobalt; however, the volume fraction of the cobalt compared to the polymer is very small.

Samples were sealed in Pyrex tubes under vacuum and annealed at temperatures up 350 °C for the crosslinked samples and 160 °C for the linear samples. Magnetic measurements were made using an alternating gradient force magnetometer and a SQUID susceptometer. In both cases, powders were loaded into a paraffin-filled polyethylene bag in an argon atmosphere. The samples were sealed into the bags and the paraffin melted to prevent magnetization rotation due to physical rotation of an entire particle. All bagged samples were stored in a vacuum dessicator.

All of the samples were ferromagnetic in their as-synthesized state, except for the linear polymer synthesized with THF, which was superparamagnetic. Table I summarizes the magnetic parameters for each of the different syntheses. The choice of polymer type and solvent produce significant variations in the magnetic properties of the four runs. Solvent selection has been shown to affect particle size in similar syntheses,[15] as has the degree of crosslinking.

TABLE I. Summary of magnetic properties of as-synthesized nanocomposites.

Run #	Crosslinking	Solvent	H_c (Oe)	M_r/M_s
33	Crosslinked	Ether	56	0.083
34	Crosslinked	Toluene	133	0.151
57	Linear	Toluene	49	0.021
58	Linear	Tetrahydrofuran (THF)	8	0.004

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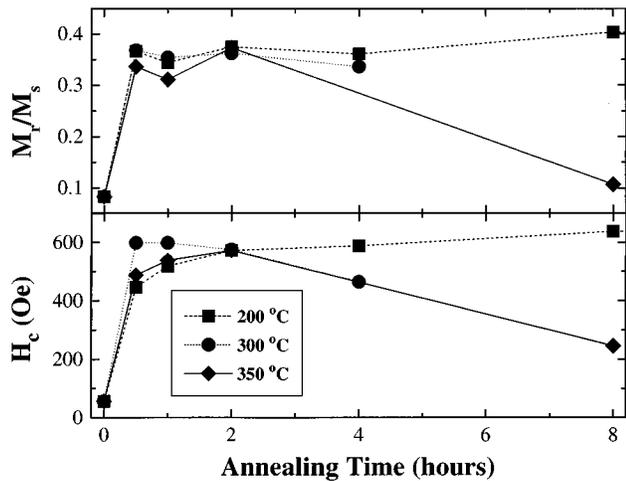[b]Department of Chemistry.

FIG. 1. The dependence of the coercivity H_c and the remanence ratio M_r/M_s on annealing time at different temperatures for Run 33 (crosslinked polymer, ether solvent).

FIG. 2. The dependence of the coercivity H_c and the remanence ratio M_r/M_s on annealing temperature for samples made with initially linear polymer. Samples made with THF are shown as squares and those made with toluene are shown as circles.

Figure 1 shows the dependence of the coercivity H_c and remanence ratio M_r/M_s on annealing time for Run 33 (crosslinked polymer, ether solvent). H_c rises rapidly from 56 to 450–600 Oe after short ($<$1 h) annealing times. Samples annealed at $T>300$ °C experience a significant decrease in coercivity after 2 h of annealing. Longer annealing times at lower temperatures result in a slight continued increase in both H_c and M_r/M_s, with values plateauing after about 10 h. Samples annealed at $T<200$ °C (not shown in Fig. 1) follow the same qualitative behavior as the data shown for annealing at 200 °C, but plateau at lower values. Similar behavior is observed for Run 34 (initially crosslinked polymer, toluene solvent). This run has a higher initial H_c, but annealing produces less of an increase in the coercivity and the remanence ratio. H_c never rises above 225 Oe and M_r/M_s is ≤ 0.2 for all annealing conditions.

The effect of solvent choice on particle size and crystallinity is not well understood. One possibility is that the solvents form protective coatings around the particles, limiting particle size. Our studies of particles synthesized without the polymer matrix suggest that the metal particles are initially crystalline on the scale of 2–5 nm, with amorphous material surrounding the crystallites. Short-time annealing slightly increases the size of the crystallites without allowing significant agglomeration. Transmission electron microscopy and mass calculations of particle syntheses without a matrix indicate that lithium, naphthalene and/or some of the solvent is retained within the particles. Annealing may vaporize trapped organics, allowing crystallite growth.

In the initially linear polymers, annealing was performed at temperatures up to 160 °C (20 °C above the glass transition temperature of the undoped polymer). H_c and M_r/M_s both initially rise with increasing annealing time, then plateau around 2–4 h, regardless of the annealing temperature. Figure 2 shows H_c and M_r/M_s as a function of annealing temperature for samples annealed for 1 h. The toluene-based samples (shown as circles) achieve maximum coercivity and remanence ratio for annealing temperatures of 125–130 °C,
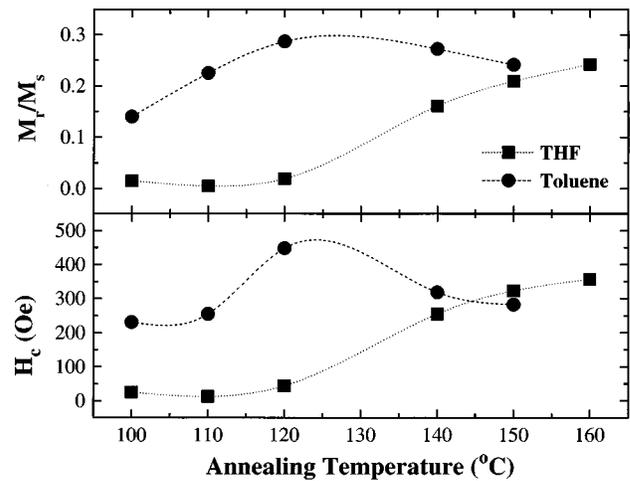
while the THF-based samples (shown as squares) display monotonically increasing values of these parameters with increasing annealing temperature.

The isothermal remanent magnetization (IRM) and dc demagnetization (DCD) have been measured to investigate the nature of the magnetic interactions. The IRM is measured from a field demagnetized state in which the initial moment is $<0.1\%$ M_s. Kelly et al.,[16] following Wohlfarth,[17] suggested that deviations from the ideal system of single-domain, noninteracting uniaxial particles will have a nonzero value of ΔM, where ΔM is defined by

$$\Delta M(H) = \frac{M^{DCD}(H)}{M^{IRM}(\infty)} - \left(1 - 2\frac{M^{IRM}(H)}{M^{IRM}(\infty)}\right). \quad (1)$$

Positive values of $\Delta M(H)$ are due to stabilizing (ferromagnetic) interactions, while negative values can be attributed to demagnetizing (antiferromagnetic) interactions. Fig-
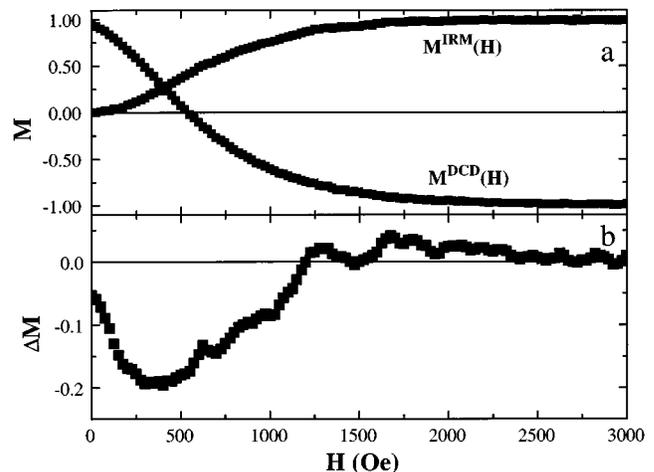

FIG. 3. (a) The isothermal remanence magnetization $M^{IRM}(H)$ and the dc demagnetization remanence $M^{DCD}(H)$. (b) The quantity ΔM, as defined by Eq. (1).
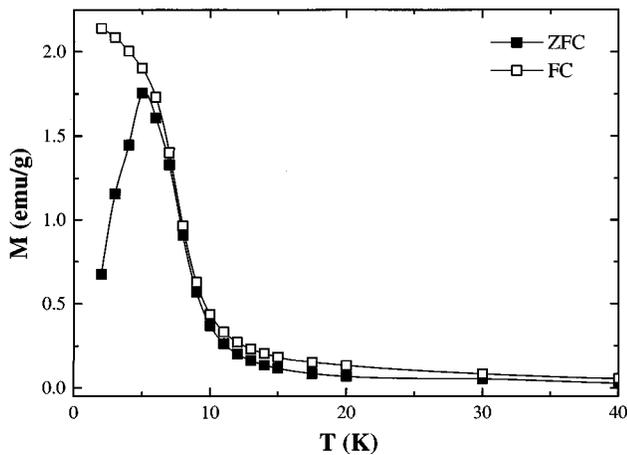
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FIG. 4. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization. The magnetization is normalized to the density of the nanocomposite.

In conclusion, we have demonstrated a synthesis technique for fabricating self-stabilized magnetic colloids consisting of cobalt nanoparticles embedded in a polymer matrix. Variation of solvent type, degree of polymer crosslinking, and annealing parameters can all significantly affect the magnetic properties. Determination of structural properties, which is complicated by the small volume fraction of cobalt to polymer, is necessary to better understand the magnetic properties. Each of the fabricated systems exhibits a cusp in the zero-field-cooled magnetization, and differences between the field-cooled and zero-field-cooled behavior. Data taken below the cusp is indicative of glassy behavior. Much work remains to better understand the properties of this novel system.

ure 3(a) shows $M^{DCD}(H)$ and $M^{IRM}(H)$ (both normalized) for a sample from Run 34 (crosslinked polymer, toluene solvent) annealed at 200 °C for 8 h. Figure 3(b), which shows $\Delta M(H)$, indicates the presence of both magnetizing and demagnetizing interactions. The predominantly demagnetizing interactions seen in Fig. 3(b) are consistent with the remanence ratio of 0.33 for this sample. The presence of both types of interactions in the same sample has been previously observed.[18,19] Contrary to the nanocomposites, particles without the polymer matrix do not exhibit evidence of any magnetizing interactions. The data shown in Fig. 3 are qualitatively representative of both crosslinked and linear polymer samples, although the ratio of magnetizing to demagnetizing interactions varies with annealing time and solvent choice.

$M(T, H = 100$ Oe$)$ is shown in Fig. 4 for field-cooled (FC) and zero-field-cooled (ZFC) measurements of an unannealed sample from Run 57 (linear polymer, toluene solvent). The undoped polymer exhibits a diamagnetic plus a Curie–Weiss magnetization with no dependence on the presence of a cooling field. The ZFC magnetization exhibits a cusp at about 5 K, with the temperature of the cusp decreasing as the interactions—measured by the remanence ratio—decrease. The width of the cusp increases in more strongly interacting systems. The FC magnetization follows the ZFC curve until a temperature of about 10 K, at which point the two curves depart and the FC curve continues to rise. As the measuring field increases, the cusp temperature decreases, and the cusp broadens and flattens. Measurements below the cusp temperature show behavior similar to that seen in glassy systems, such as spin glasses and frozen ferrofluids with random anisotropy;[20] however, more detailed, systematic measurements are required to determine the nature of the phenomena producing the cusp.

[1] R. F. Ziolo, E. P. Giannelis, B. Weinstein, M. P. O'Horo, B. N. Ganguly, V. Mehrotra, M. W. Russell, and D. R. Huffman, Science **257**, 219 (1992), and references therein.
[2] J. Eastman and R. W. Siegel, Research and Development, January, 56 (1989); R. W. Siegel, Nanostructured Mater. **4**, 121 (1994); H. Gleiter, Prog. Mater. Sci. **33**, 223 (1989).
[3] J. P. Chen, K. M. Lee, C. M. Sorenson, K. J. Klabunde, and G. C. Hadjipanayis, J. Appl. Phys. **75**, 5876 (1994).
[4] M. E. McHenry, S. A. Majetich, M. DeGraef, J. O. Artman, and S. W. Staley, Phys. Rev. B **49**, 11358 (1994); M. E. McHenry, Y. Nakamura, S. Kirkpatrick, F. Johnson, S. A. Majectich, and E. M. Brunsman, in *Fullerenes: Physics, Chemistry, and New Directions VI*, edited by R. S. Ruoff and K. M. Kadish (The Electrochemical Society, Pennington, NJ, 1994), p. 1463.
[5] T. Ambrose, A. Gavrin, and C. AL. Chien, J. Magn. Magn. Mater. **116**, L311 (1992).
[6] C. Laurent, D. Mauri, E. Kay, and S. S. P. Parkin, J. Appl. Phys. **65**, 2017 (1989).
[7] A. Singh, M. Markowitz, and G. M. Chow, Nanostructured Mater. **5**, 141 (1995).
[8] L. Yiping, G. C. Hadjipanyayis, C. M. Sorenson, and K. J. Klabunde, J. Appl. Phys. **69**, 5141 (1991).
[9] R. D. Rieke, Crit. Rev. Surf. Chem. **1**, 131 (1991), and references therein.
[10] D. L. Leslie-Pelecky, X. Q. Zhang, G. L. Krichau, and R. D. Rieke, Proc. Chem. Soc. Div. Polym. Mater. Sci. Eng. **73**, 66 (1995).
[11] J. P. Chen, K. M. Lee, C. M.Sorenson, K. J. Klabunde, and G. C. Hadjipanayis, J. Appl. Phys. **75**, 5876 (1994).
[12] R. F. Ziolo, E. P. Giannelis, and R. D. Shull, Nanostructured Mater. **3**, 85 (1993).
[13] A. Etawansi, N. Kinawy, and M. Emitwally, J. Mater. Sci. **24**, 2497 (1989).
[14] J. Yacubowicz and M. Narkis, Poly. Eng. Sci. **30**, 469 (1990).
[15] S. S. Kher and R. Wells, Chem. Mater. **6**, 2056 (1994).
[16] P. E. Kelly, K. O'Grady, P. I. Mayo, and R. W. Chantrell, IEEE Trans. Magn. **MAG-25**, 3881 (1989).
[17] E. P. Wohlfarth, J. Appl. Phys. **29**, 595 (1958).
[18] P. I. Mayo, A. Bradbury, R. W. Chantrell, P. E. Kelly, H. E. Jones, and P. R. Bissell, IEEE Trans. Magn. **MAG-26**, 229 (1991).
[19] P. I. Mayo, R. M. Erkkila, A. Bradbury, and R. W. Chantrell, IEEE Trans. Magn. **MAG-26**, 1894 (1991).
[20] W. Luo, S. R. Nagel, R. F. Rosenbaum, and R. E. Rosenzweig, Phys. Rev. Lett. **67**, 2721 (1991).