

Solid containing rotationally free nanocrystalline γ -Fe₂O₃: Material for a nanoscale magnetic compass?

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A nanocomposite material has been characterized that contains nanometer size magnets that are free to rotate in response to an applied magnetic field. The composite consists of 5–10 nm crystals of γ -Fe₂O₃ dispersed in a solid methanol polymer matrix. The material was prepared by freezing a methanol-based ferrofluid of γ -Fe₂O₃ and subjecting it to a magnetic field applied in alternate directions to anneal the matrix. Before the field treatment, the solid displays magnetic behavior characteristic of an ordinary nanoscopic magnetic material. It is superparamagnetic above the blocking temperature (160 K) and hysteretic below, showing magnetic remanence and coercivity. After the field treatment to anneal the matrix, the same solid shows only Curie–Weiss behavior above and below the blocking temperature over the temperature range from 4.2 to 200 K and in response to applied magnetic fields as low as 1.59 kA/m. The data are consistent with a solid containing rotationally free, nanoscopic magnets encased in cavities of very small dimensions. The free rotation of the particles precludes the observation of magnetic relaxation phenomena that are characteristic of magnetic solids and ferrofluids. The present solid portends a class of magnetic materials with very little or no electrical and magnetic loss. © 2000 American Institute of Physics. [S0021-8979(00)06911-5]

I. INTRODUCTION

In contrast to colloidal dispersions, nanoparticles dispersed in solids are generally assumed to be locked in place and to possess little if any mechanical freedom. The design of solids containing mechanically free nanoparticles in small cavities could lead to intelligent materials with unexpected properties for use in acoustical, electrical, magnetic, mechanical, optical and thermal applications.

It is generally recognized that nanoscopic materials possess unique physical and chemical properties which, in some cases, may be attributed to quantum confinement effects in the nanoparticulate.¹ It now appears possible to change the properties of these materials by altering the matrix in which the particles are either made or dispersed. Modifying the matrix, for example, could lead to changes in the composition, morphology, size, distribution, and attitude of the particulate, in the matrix–particle interaction, or in the micro- or nanostructure of the composite itself.^{2–6} Earlier, we demonstrated that nanocrystalline γ -Fe₂O₃ could be isolated in an ion exchange resin to produce a nanocomposite with novel optical and magnetic properties.^{2,7} We have now modified the resin matrix to provide a nanocomposite containing rotationally free, nanometer sized magnets.⁸ The material displays magnetic behavior and prototypes a generation of nanoscale materials whose potential applications include electronic circuitry, sensor, switch, generator, motor, electrical transformer, and heat transfer management technologies.

II. PROCEDURE

A methanol-based ferrofluid containing 8.8% by weight solids and 2.1% iron was prepared by micronizing a nanocomposite containing 57% by weight γ -Fe₂O₃ in a 4% cross-linked sulfonated polystyrene ion exchange resin^{2,7} (Fig. 1). Typically, 2 g of the nanocomposite were placed in a 4 oz, wide-mouth jar (4.5 cm o.d.) with 300 g of 1/4 inch 440 stainless steel shot. The contents of the jar were roll milled for 120 h in the dry state and then again for 16 h after the addition of 40 ml of methanol. The resulting fluid was centrifuged at 8500 g for four, 15 min intervals. The fluid was then concentrated to 10 ml by ultrafiltration in an Amicon 8200 stirred cell under 36 psi of nitrogen using a cellulose membrane with an average pore size of 40 nm. The ferrofluid was characterized by electron microscopy and magnetometry (Fig. 2) using a superconducting quantum interference device (SQUID) magnetometer and a sealed Kevlar sample holder.

The sample, while still in the magnetometer, was then subjected to the following matrix annealing treatment to produce the free-rotor nanocomposite. The ferrofluid was cooled to 4.2 K in the absence of a magnetic field then briefly exposed to an applied magnetic field of +400 kA/m and then –400 kA/m. Next, the sample was subjected to a gradually increasing, alternating applied magnetic field as depicted in Fig. 3, which plots magnetization as a function of applied magnetic field strength. Numbers 1–4 indicate the sequence in which the applied field was varied.

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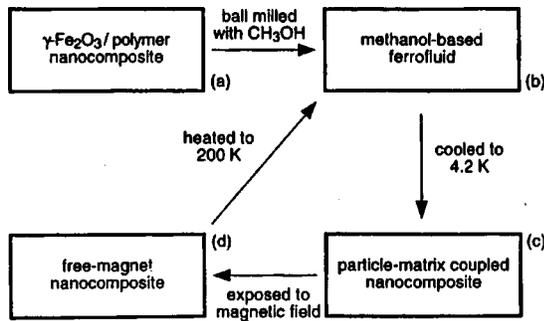


FIG. 1. Diagram for the preparation of the free-rotor composite.

III. RESULTS AND DISCUSSION

At room temperature, the methanol-based ferrofluid is thixotropic; upon standing, it gels, then undergoes reversible liquefaction upon shaking. Transmission electron microscopy with selected area electron diffraction of the ferrofluid residue after evaporation showed 5–10 nm crystallites of $\gamma\text{-Fe}_2\text{O}_3$ unchanged from those of the starting material. Representative photomicrographs of the particles appear elsewhere.^{2,7}

Magnetic characterization of the ferrofluid before treatment to form the free-rotor composite showed temperature and field dependent magnetization curves (Fig. 2) typical of ultrafine particle magnetic composites. The low field magnetization M versus temperature T measurements for the zero-field-cooled (ZFC) and field-cooled (FC) cases reveal the existence of irreversibility phenomena commonly associated with metastable magnetic states. The broad peak in the ZFC curve is due to the broad distribution of energy barriers and relaxation times of the magnetic moments of the particles. The maximum in the ZFC data at 160 K is the blocking temperature T_b , which corresponds to the blocking of the magnetic moment of the particles with random orientations of the anisotropy direction. Similar behavior is observed for nanocrystalline $\gamma\text{-Fe}_2\text{O}_3$ in the solid polymer.^{2,3,7}

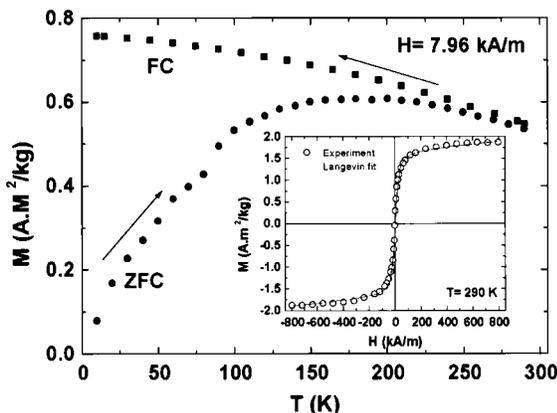


FIG. 2. Magnetization M vs temperature T curves for the FC and ZFC cases for the fixed particle (matrix locked) sample in an applied field of 7.96 kA/m. Inset shows magnetization M vs applied field H for the sample (ferrofluid) at room temperature along with the Langevin fit.

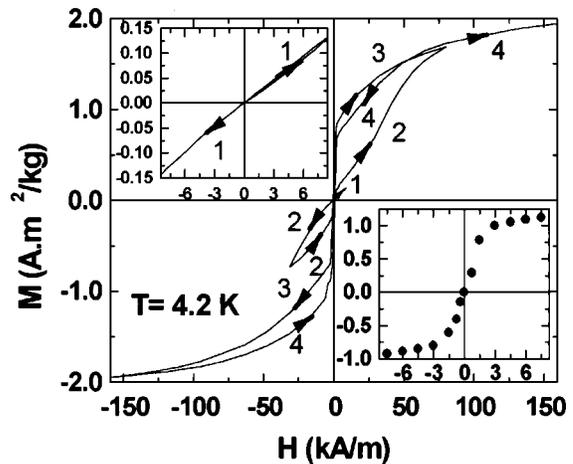


FIG. 3. Evolution of the free rotor system in four steps. Magnetization M vs applied field H curves at 4.2 K recorded between -150 and $+150$ kA/m as follows: (step 1) $H=0.0$ to 0.0 to 7.96 ; (step 2) $H=-7.96$ to -31.8 to 0.0 to 79.6 ; (step 3) $H=79.6$ to 0.0 to -159.2 ; (step 4) $H=-159.2$ to 0.0 to 159.2 kA/m. Inset (a) displays the magnetization curve obtained in step 1. Here the magnetization at $H=7.96$ kA/m, approximately 0.13 A m²/kg, indicates that the particles are matrix coupled in the frozen state. Inset (b) represents the magnetization curve obtained in step 4. Here, saturation was reached at a field $H=3.2$ kA/m; the magnetization at $H=7.96$ kA/m, approximately 1.12 A m²/kg, is much larger than that obtained in step 1 in the same field, indicating the particles are free to rotate.

The variation of the magnetization with applied field H at constant temperatures above T_b shows the absence of remanence and coercivity characteristic of superparamagnetic materials.^{2,3,7,9} Below T_b , the sample shows the characteristic hysteresis loop in the magnetization vs field curves. At room temperature (Fig. 2 inset) the ferrofluid is liquid and superparamagnetic, consistent with the presence of crystalline $\gamma\text{-Fe}_2\text{O}_3$ above the blocking temperature.

After the sample is frozen at 4.2 K and subjected to the alternating 400 kA/m field treatment, the magnetic characteristics of the sample change significantly as shown in Fig. 3. Although the sample is well below the blocking temperature, the data show no coercivity throughout the applied field treatment over the four sequential steps. This behavior is in contrast to the sample's behavior before the field treatment shown in Fig. 2 (vide supra). At the same time, however, the data show irreversibility attributable to the random directions of the magnetic moments of the particles in the matrix, which in turn depend on the magnetic history of the sample. We note that very small fields produce a full reversal of the total magnetic moment of the system as depicted in the insets, (Fig. 3). These data suggest the possibility that the magnetic particles are free to rotate in the matrix in response to the applied magnetic field. In the absence of matrix annealing with the 400 kA/m cycle, the sample followed the behavior shown in Fig. 2.

Temperature dependent, low field magnetization measurements were carried out on the sample to further test for the presence of free rotor magnets. After the field treatment indicated in Fig. 3, the sample was gradually warmed in an applied field of 1.59 kA/m while monitoring the magnetization. The resultant behavior, shown in Fig. 4, is completely different from that observed for the sample before field treat-

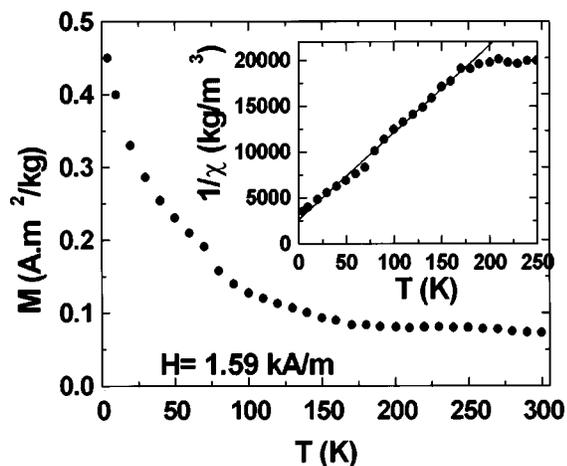


FIG. 4. Magnetization M vs temperature T curve for the free-magnet nanocomposite at 1.59 kA/m after the final step, 4, in Fig. 3. The inset displays inverse magnetic susceptibility as a function of temperature, showing Curie–Weiss behavior for the nanocomposite.

ment, Fig. 2. Instead, the magnetization versus temperature dependence of the field-treated sample is now typical of that for a paramagnetic system showing Curie or Curie–Weiss behavior. The data indicate that there are no barriers to the orientation of the magnetic moments of the particles in the direction of the applied magnetic field. Since the anisotropy constant of the particles must be nonzero, the data in Fig. 4 further demonstrate the existence of the free-rotor magnet, that is, each particle with its magnetic moment rotates freely in the matrix in the presence of an applied magnetic field. The behavior is observed from 4.2 to 200 K. Above 200 K, the solid melts to reform the ferrofluid. When the entire procedure is repeated, the sample displays the same behavior (Fig. 1). The magnetic data indicate the absence of viscosity effects normally seen in ferrofluids and other magnetic colloids where particle rotation is damped by the viscosity effects of the medium. Below the freezing point of oxygen (55 K), the particles presumably exist in a partial vacuum.

The variation of the inverse magnetic susceptibility with temperature is shown in the inset, Fig. 4. The nearly linear dependence observed up to 175 K is close to the Curie–Weiss behavior typical of free spins. This behavior is expected above the blocking temperature, i.e., in the superparamagnetic regime, since the Curie–Weiss behavior of the magnetization is a consequence of the fact that the thermal energy is larger than the barriers against the change in the direction of the magnetic moment. Here, the characteristic reversal time for the magnetic moment of the major part of the particles is smaller than the experimental resolution time.

Below the blocking temperature of the particles, the magnetic moments of the particles are blocked for a time that increases exponentially with decreasing temperature. The observation of Curie–Weiss law behavior for the sample at low temperatures demonstrates the absence of barriers between the different directions of the magnetic moments of the particles. This can only happen if the magnetic moment of each particle is always aligned with the easy axis and the rotation of the magnetic moment is accompanied by the rotation of the particle in the presence of the applied field.

The plateau in the χ^{-1} vs T plot (Fig. 4) may indicate a glass transition temperature for the polymer methanol mixture. The low temperature end of the plateau coincides with the freezing point of methanol, 175 K. The discontinuity in the χ^{-1} vs T curve between 75 and 85 K for the decoupled material coincides with that in Fig. 2, observed in the M vs T curve of the coupled material in the zero field case. The discontinuity may indicate a phase transition in the matrix, which presumably remains unchanged in the field-treated, free rotor system.

The negative Curie–Weiss intercept may indicate some residual magnetic dipolar interaction between the particles. We estimate the particle–particle dipolar field to be approximately 1 Oe, which is consistent with interactions between particles. Other factors which possibly contribute to the non-zero value of the Curie–Weiss temperature include frictional interactions between the particles and the matrix, a small population of nonrotors or matrix-locked particles, and the occupancy of more than one particle per cavity. None of these possibilities has been ruled out. In the absence of frictional and magnetic dipolar interactions, the time dependence of rotation depends only on the inertial moment and mass of the particle. Thus, in the case of the ideal nanoscale particle, rotation would be expected to take place at about 10^6 – 10^9 Hz.

The mechanism of free-rotor formation for the present material is unknown. Its formation, however, appears to be an evolutionary process, which starts with the 400 kA/m cycle to anneal the matrix. It then continues through the torquing action of the applied magnetic field in one direction and then the other, taking the composite from the particle-locked to the particle-free state. One possibility is that the methanol polymer matrix, particularly within the vicinity of the particle, is of a cavernous and friable nature. In this case, application of the higher field (400 kA/m) could cause an initial fracturing of the matrix in the vicinity of the particle. Upon application of the alternating lower field treatment (Fig. 3), particles begin to break from the matrix proper, possibly to further define a cavity.

Generally, magnetic nanocomposites would not be expected to form free-rotor systems with the field treatments reported here. In the present case, however, independent studies suggest that the matrix in the vicinity of the particle plays a critical role in determining the properties of the nanocomposite.^{2,4,7,12} The role may be critical in the case of the free rotors as well. In a separate study, we prepared and characterized a second nanostructured material containing rotationally free magnets in a methanol polysaccharide matrix.¹¹ Unlike the water based ferrofluid, the precursors to both methanol polymer free rotor systems form thixotropic gels that involve solvent-swollen polymer networks surrounding the magnetic particles.¹² Additionally, both systems show behavior similar to that of the so called “smart” gels.^{12,13} In the liquid and gel phases, the ensuing structures may involve entropy-driven ordering¹⁴ and interconversions between ionic, hydrophobic, and hydrogen bonding interactions. We believe that such interconversions play a critical and enabling role in the formation of the present free-rotor systems. We note that a water-based ferrofluid prepared un-

der conditions similar to the methanol-based ferrofluid did not form a free-magnet composite after cooling and field treatment.

Evidence from the polysaccharide free rotor system¹¹ suggests that the particle matrix surfaces are mutually antagonistic. Such behavior is not unusual for hydrogel materials.¹³ In the present case, the physical movement of the particle caused by the torque resulting from the 400 kA/m field treatment would be sufficient to convert the particle matrix interaction from one involving weak hydrogen bonding to one involving mutually antagonistic, i.e., hydrophobic and hydrophilic, surfaces. The particles would then be free to rotate as observed with application of the weaker fields. Free rotor studies with additional matrices (*vide infra*) are in progress.

A comparison of the magnetic behavior of a fixed-particle versus ideal free-rotor magnetic nanocomposite is summarized in Figs. 5(a)–5(e). The uniqueness of free-rotor magnetic nanocomposites rests in the absence of time-dependent phenomena with changes in an applied magnetic field. Hysteresis is absent because the particles physically rotate in response to the field. On the other hand, matrix-locked magnetic particles show dissipation phenomena, such as Néel relaxation at high temperatures and quantum tunneling of magnetization (QTM) at low temperatures. As a consequence of the latter, the north and south poles of a nanometer magnet can spontaneously interchange.¹⁵ In a free-rotor system, however, QTM cannot occur because of the conservation of total angular momentum.¹⁶ The latter obligates that changes in the direction of the magnetic moment, intrinsic angular momentum, or spin, induce rotational motion of the particles. In the ideal case, such a material would be a potential sensor for use in low-temperature antenna experiments to detect gravitational waves since it would produce no magnetic noise.

The saturation magnetization M_s of the present composite may be increased or decreased by changing the composition or the particle number density of the magnetic species. The latter may be accomplished by at least two methods, including concentrating the ferrofluid and increasing the particle loading of the starting material as described earlier.^{2,12} Aside from the near total absence of magnetic and electrical losses, and of thermal magnetic relaxation, the new composites have a density of about 1000 kg/m³ and are electrically insulating. These characteristics and the ability to adjust M_s , suggest many potential applications for the nanocomposite, including that of a “three-dimensional” magnetic nanocompass or gyro. The idealized magnetic behavior depicted in Fig. 5(g), for example, suggests applications in sensor and switch technology,¹⁷ electrical transformers, motors, and generators and in magnetic refrigerant and heat transfer management technology. Free-rotor magnetic composites may also offer the possibility of providing soft magnet materials with permeabilities approaching those of the best known alloys.¹⁸ Other matrices, such as zeolites, fullerenes, nanotubes, layered structures, clathrates, polymers, and cellular solids¹⁹ may prove useful in the synthesis of free-rotor materials.

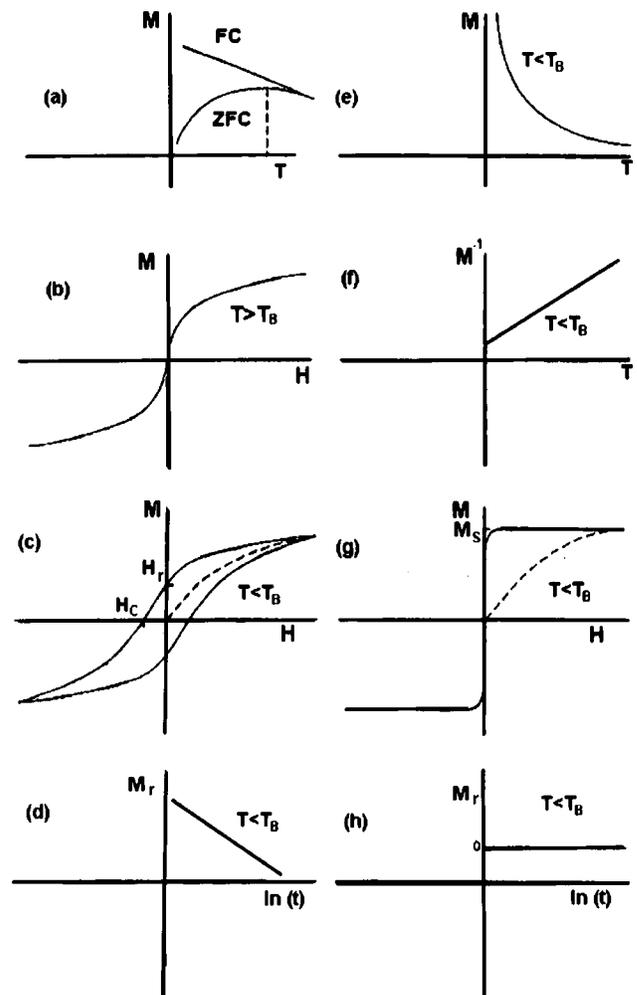


FIG. 5. Comparison of the magnetic behavior of a matrix-fixed vs ideal free-rotor magnetic nanocomposite. M , H , T , T_b , M_r , H_c , and M_s represent the magnetization, applied field, temperature, blocking temperature, remanence, coercivity, and saturation magnetization, respectively. In the particle–matrix coupled case, (a)–(d) the system is superparamagnetic, showing: (a) irreversibility for the FC and ZFC cases; (b) zero hysteresis when $T > T_b$; (c) hysteresis when $T > T_b$ and (d) logarithmic time dependence of the remanence, i.e., magnetic relaxation as a manifestation of the existence of energy barriers. In the free magnet or particle–matrix decoupled case below the blocking temperature (e)–(h), the system is paramagnetic showing: Curie–Weiss (or Curie) behavior (e) and (f); (g) the absence of remanence and coercivity, and (h) the absence of magnetic relaxation. The dashed curve in (g) represents the initial magnetization of the system before all of the particles are free to rotate.

We note that other nanocomposite materials containing free particles, whether magnetic or nonmagnetic, may exist in the laboratory and nature, but have gone undetected. In the case of magnetic nanorotors if the blocking temperature, as measured by dc magnetometry, is below the measurement temperature, the presence of a free rotor would be masked by the apparent superparamagnetic behavior of the material and, therefore, go undetected. Rotating magnets have been proposed as the basis of a theoretical model for a biological magnetoreceptor.²⁰

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