Preparing polymer films doped with magnetic nanoparticles by spin-coating and melt-processing can induce an in-plane magnetic anisotropy

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Faraday rotation has been used to investigate a series of polymer films doped with magnetic iron oxide nanoparticles. The films have been prepared by spin-coating and melt-processing. In each case, upon varying the angle of optical incidence on the films, an in-plane magnetic anisotropy is observed. The effect of such an anisotropy on the Faraday rotation as a function of the angle of optical incidence is verified by comparison with magnetically poled films. These results demonstrate that care should be taken upon analyzing the magnetic behavior of such films on account of the sample preparation techniques themselves being able to affect the magnetization. © *2011 American Institute of Physics*. [doi:10.1063/1.3572048]

Due to their relatively low cost, superior magnetic properties, and ease of processing, magnetic nanoparticles are an interesting candidate for highly efficient Faraday materials.[1,2] In particular, incorporating these nanoparticles into a polymer matrix offers control over the interparticle distance and improves optical transmission.[3] Further, the resulting material presents additional degrees of tunability, as its magnetization can be manipulated by external stimuli, such as thermal, electric, magnetic, or mechanical effects and, from a practical point of view, it is very straightforward to handle. In practice, samples are typically prepared by introducing the nanoparticles into a polymer solution/melt and subsequently processed via drop casting, spin-coating, Langmuir–Blodgett technique, layer-by-layer assembly, etc.[4] However, because of this material's relatively high susceptibility to external mechanical stimuli, could not the sample preparation method itself affect the magnetization?

In this communication, we make use of Faraday rotation to demonstrate that upon preparing thin films of Fe_3O_4 nanoparticles within a polymer matrix, the mechanical forces that occur in the plane of the film during sample preparation can induce an in-plane magnetic anisotropy. The effects of this anisotropy are compared with those, induced by an externally applied magnetic field during sample preparation. Both the mechanically and the field-induced magnetic anisotropies likely arise from collective nanoparticle properties, which are due to reduced interparticle distances.

The nanoparticles were prepared by the forced hydrolysis method. The salt precursor was analytical grade anhydrous $FeCl_3$, the solvent was ethylene glycol, and octylamine was the capping agent.

In a typical synthesis, 37.5 ml of ethylene glycol and 25 ml octylamine were introduced into a 100 ml round bottom flask and heated to 150 °C. Then 2.4 g $FeCl_3$ was added to 10 ml ethylene glycol and 4 ml MilliQ water. After stirring, this solution was added drop-wise to the heated round bottom flask and further heated to reflux at 185 °C for 18 h.

After cooling, the nanoparticles were washed with acetone, precipitated by means of our homemade magnet and redispersed via sonication. This process was then repeated four times, after which the nanoparticles were dried in a vacuum oven. A typical synthesis yields around 1 g of nanoparticles.

The solutions for the preparation of the spin-coated films were made using chloroform as solvent. Each solution was treated in an ultrasonic bath for at least 2 h before deposition. The time between sonication and sample preparation was minimized to insure the best dispersion. During spin-coating, the disk rotates at 3000 rpm and the polymer spreads within a fraction of a second; the chloroform solution evaporates within 5 seconds.

The solvent used for the melt-processed films was also chloroform but it was left to evaporate while sonicating, again to ensure the best dispersion. The last traces of chloroform were then removed in an oven, which was heated at 130 °C. The resulting "nanoparticle-doped polymer" is heated above the glass transition temperature, to 170 °C, and it is pressed between two BK7 glass plates for 30 sec. The cooling takes 120 sec. Spacers inserted between the plates ensure a uniform thickness for the melt-processed films. BK7 glass was used because of its standard ion content, and hence very consistent Faraday rotation, making it an ideal substrate.

Faraday rotation was measured in an ac magnetic field configuration with a home-made setup, described in Refs. 5 and 6. Transmission electron microscopy (TEM) was performed on samples deposited on a holey carbon grid. The

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measurements were performed using a JEOL 4000EX microscope operating at 400 kV and having point resolution of 0.17 nm.

Figure 1(a) shows a high-resolution TEM image of a single Fe_3O_4 nanoparticle and a Fourier transform pattern is given in the inset. Both demonstrate a perfect crystalline structure, almost free of defects, and a good octahedral shape. It should be pointed out that Fe_3O_4 has a cubic crystalline structure and that, consequently, there should be three easy axes of magnetization. However, due to shape anisotropy, for instance expressed through truncated planes, one of these axes becomes dominant and, therefore, an individual nanoparticle can be regarded as having uniaxial magnetic anisotropy.

Upon examining a large collection of nanoparticles, as in Fig. 1(b), we can see that the magnetic anisotropy averages out. Indeed, in Fig. 1(b), the nanoparticles, and therefore their easy axis of magnetization, are randomly oriented. Further, there are variations in shape, which imply variations in magnetic shape anisotropy, as well as variations of size, which imply variations in magnetic order—superparamagnetic versus ferrimagnetic. More specifically, the diameter of the nanoparticles is, on average, 14.33 nm, with 66% of the nanoparticles between 11.17 and 18.37 nm, and 98% of the nanoparticles between 7.90 and 25.98 nm. The superparamagnetic limit, at room temperature, for Fe_3O_4 nanoparticles is often situated at approximately 20 nm,[4,7] although values of up to 25 nm have been cited.[8]

In our Faraday rotation experiment, the beam diameter was 2 mm and, henceforth, the magnetic response, which is expected from the nanoparticles upon rotating the sample, is isotropic. A schematic diagram of the Faraday rotation experiment is shown in Fig. 2(a). The rotation angle of the polarized light is given by $\varphi = VdB$, where V is the Verdet constant, d is the sample thickness, and B is the magnetic flux density in the direction of propagation. Upon rotating the sample, the angle that forms between the direction of propagation and the z axis is α. We have chosen a coordinate system on the sample, such that the x and y axes lay in the sample plane, whereas the z axis is perpendicular to it. Henceforth, rotating the sample is equivalent to varying α, the angle of optical incidence. It should be noted that upon increasing α, the Faraday rotation will increase due to the increase in sample thickness d along the direction of propagation. This increase in d is a direct consequence of the Snell–Descartes law. In fact, for a sample with an isotropic magnetization, upon varying α, there should be no other increase in the Faraday rotation. But what if the magnetization is not isotropic?

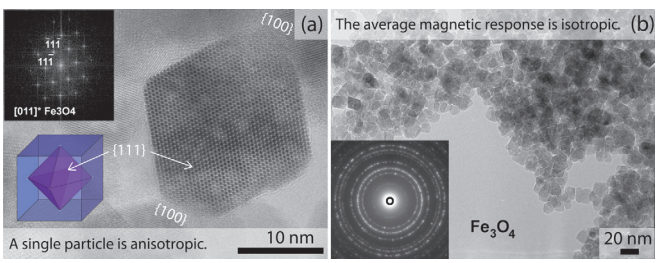

FIG. 1. (Color online) The magnetic anisotropy of single particles is averaged out over a large amount of randomly oriented particles. (a) High-resolution transmission electron microscopy (TEM) image and the corresponding Fourier transform pattern (inset) demonstrate the good crystalline order of a [011]-orientated Fe_3O_4 nanoparticle. (b) Low-resolution TEM image of a collection of nanoparticles and the corresponding electron diffraction pattern (inset) confirm the cubic structure order in the nanoparticles on a larger scale. Due to differences in size, shape, and orientation of the nanoparticles, the average magnetic response is isotropic.

The Stoner–Wohlfarth model is the simplest model that describes adequately the physics of a magnetic particle with a single axis of anisotropy.[9] In Figs. 2(b) and 2(c), we consider two possible directions for this anisotropy, in- and out-of-plane, respectively. We can therefore write an effective anisotropy such as

$$K_{\text{eff}} = 2\pi M_S^2 \left(N_{\parallel} - N_{\perp}\right), \tag{1}$$

where M_S is the saturation magnetization, while $N_{\parallel}$ and $N_{\perp}$ are the demagnetization coefficients, in- and out-of-plane, respectively.

The energy for this system results from the competing effects of the anisotropy energy $K_{\text{eff}} \sin^2\theta$ and the Zeeman energy $-\mathbf{M}\cdot\mathbf{H}$. Consequently the energy can be expressed as

$$E = K_{\text{eff}} \sin^2\theta - M(H\sin\alpha\cos\theta + H\cos\alpha\sin\theta), \tag{2}$$

where θ is the angle between the direction of magnetization and the y axis. In order to determine θ, we can plot Eq. (2) for different values of α and H. The minima of the energy indicate then the direction of magnetization. In order to estimate the effect on the Faraday rotation, we can then plot M_H—the component of the magnetization along the direction of $\mathbf{H}$—as a function of $\mathbf{H}$. In Fig. 2(d), such a plot can be seen, where both variables have been normalized by their saturation values. Clearly, although for an out-of-plane anisotropy we can see that M_H *decreases* as a function of α, for the in-plane anisotropy M_H *increases* as a function of α. We can directly compare these simulation trends with Faraday rotation experiments.

For the purpose of this comparison, magnetic in- and out-of-plane anisotropies are induced in melt-processed films by the poling procedure: in the presence of 0.4 T externally applied magnetic field (in- or out-of-plane), the films are first heated above their glass transition temperature and then allowed to cool down. The resulting anisotropy has a pronounced effect on Faraday rotation experiments.[10,11]

In Fig. 3(a), the Faraday rotation is given as a function of the angle α. To allow a clearer comparison with the idealized simulations in Fig. 2(d), the Faraday rotations for both in- and out-of-plane anisotropies are normalized to 0 and 1, respectively. Further, we removed the Snell–Descartes dependence from the results and it should be noted that the contribution from the BK7 glass plates amounted to approximately 5% of the signal. Additionally, BK7 glass is unaffected by the poling. It is then immediately apparent that the experimental data are in very good qualitative agreement with the simulations, i.e., that the Faraday rotation increases with α for the in-plane anisotropy, whereas it decreases with α for the out-of-plane anisotropy. In principle, in the absence of anisotropy, the Faraday rotation should remain constant as a function of α. However, as we can see in Fig. 3(a), the sample that was not poled exhibits a behavior that suggests the

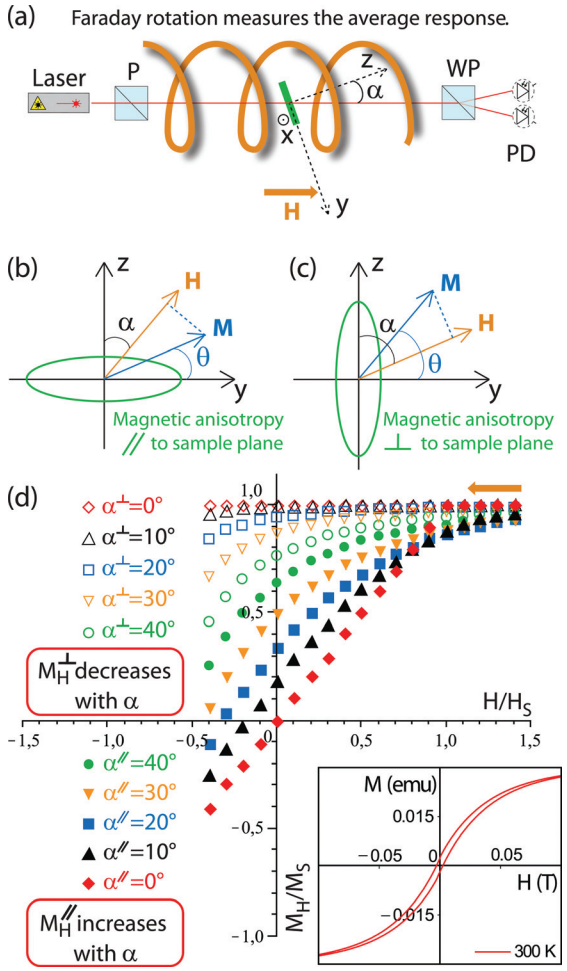

FIG. 2. (Color online) Sample preparation can induce a magnetic anisotropy. (a) The schematic diagram of a Faraday rotation experiment, whereby the average magnetic response of a sample is measured. The sample contains Fe_3O_4 magnetic nanoparticles within a polymer poly(isobuthylmethacrylate) PBMA matrix. Due to the sample preparation procedure, a magnetic anisotropy can be induced, for instance, in the plane of the sample (b) or perpendicular to it (c). The magnetic behavior can then essentially be described by the Stoner–Wohlfarth model for one "effective" magnetic particle, having one axis of anisotropy. (d) Normalized simulation results for the component of M_H—the magnetization along the direction of applied magnetic field—as a function of the applied magnetic field (**H**), for different angles of optical incidence on the sample (α). The data are calculated from the positive saturation field (H_S) downward, along the first reversal of the hysteresis loops, as indicated by the arrow. In the inset, a vibrating sample magnetometer measurement shows the hysteresis loop, at room temperature, from the nanoparticles within a PBMA matrix, *before sample preparation*.

presence of an in-plane magnetic anisotropy. What is the origin of this anisotropy?

The inset in Fig. 3(a) shows a schematic representation of the melt-processing sample preparation procedure. It can be seen that during the procedure, the film is subjected to in-plane mechanical forces. Such in-plane forces are also applied to the film during spin-coating, see inset in Fig. 3(b). If the mechanical forces are responsible for the magnetic in-plane anisotropy, then a nonpoled spin-coated sample should also present signs of in-plane magnetic anisotropy in its Faraday rotation response as a function of the angle of incidence, α. In fact, this is indeed the case, as Fig. 3(b) demonstrates. Therefore, both external magnetic field and mechanical forces on the sample can induce magnetic anisotropies. In the case of an applied external magnetic field, the nanoparticles are oriented with their easy axis along the direction of that field. In the process, the distance between nanoparticles is reduced and under the influence of dipole–dipole interactions, collective properties are induced.[12] A similar mechanism is likely occurring under the influence of mechanical forces as it has been shown that the centrifugal forces and flow during spin-coating, is able to induce anisotropy in films composed of highly rigid structures.[13–15]

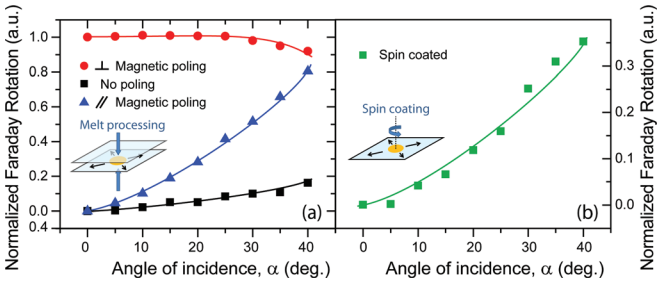

FIG. 3. (Color online) The measured Faraday rotation is in good qualitative agreement with the theoretical simulations. (a) The Faraday rotation increases or decreases as a function of the angle of optical incidence, for in- or out-of-plane magnetic poling—cooling the sample in the presence of magnetic field during melt-processing. Even in the absence of magnetic poling, this sample preparation procedure itself can induce a slight in-plane magnetic anisotropy. (b) Upon preparing the samples by spin-coating Poly(-methyl methacrylate) (PMMA), the induced in-plane magnetic anisotropy is significantly larger. The lines are guides to the eye.

Because polymer films are sensitive to various external stimuli, dispersing magnetic nanoparticles within them result in a material, where the magnetization can be tailored by means of these same external stimuli. However, we have shown that this enhanced functionality could also constitute a limiting factor; as the magnetization can be affected by the film production procedure itself. We have made use of both the spin-coating and the melt-processing procedures and we have evidenced the appearance of an in-plane magnetic anisotropy in polymer films hosting Fe_3O_4 nanoparticles. Our results suggest that other procedures and combinations of materials should be investigated for similar effects.

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[1]A. K. Zvezdin and V. A. Kotov, *Modern Magnetooptics and Magnetooptical Materials* (IOP, Bristol, 1997).
[2]L. L. Beecroft and C. K. Ober, Chem. Mater. **9**, 1302 (1997).
[3]R. F. Ziolo *et al.*, Science **257**, 219 (1992).
[4]S. P. Gubin, *Magnetic Nanoparticles* (Wiley, Hoboken, NJ, 2009).
[5]V. K. Valev, J. Wouters, and T. Verbiest, Eur. J. Phys. **29**, 1099 (2008).
[6]V. K. Valev, J. Wouters, and T. Verbiest, Am. J. Phys **76**, 626 (2008).
[7]D. Caruntu, G. Caruntu, and C. J. O'Connor, J. Phys. D: Appl. Phys. **40**, 5801 (2007).
[8]S. Thomas *et al.*, Nanotechnology **17**, 5565 (2006).
[9]C. Tannous and J. Gieraltowski, Eur. J. Phys. **29**, 475 (2008).
[10]S. I. Stupp, H. C. Lin, and D. R. Wake, Chem. Mater. **4**, 947 (1992).
[11]X. Qiao *et al.*, J. Soc. Rheol. Jpn. **38**, 23 (2010).
[12]M. P. Pileni, J. Phys. Chem. B **105**, 3358 (2001).
[13]G. Koeckelberghs *et al.*, Adv. Mater. **17**, 708 (2005).
[14]W. M. Prest and D. J. Luca, J. Appl. Phys. **51**, 5170 (1980).
[15]D. McBranch *et al.*, Appl. Phys. Lett. **66**, 1175 (1995).