

Role of magnetostatic interactions in assemblies of Fe nanoparticles

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It has recently become possible to synthesize a class of nanostructured materials by ion implantation. The implanted ions aggregate into crystallographically oriented nanoscale inclusions in the host material. We have performed simulations of the magnetization curves for such assemblies of nanoscale Fe inclusions in a nonmagnetic host. We use random positions for the magnetic particles (not a regular grid) and include magnetostatic interactions in detail. We find that these materials are not adequately described by standard noninteracting theories—interactions have a significant effect. In particular, interactions can mask the effects of crystallite orientation, producing nearly isotropic hysteresis curves. The use of a noninteracting model could thus lead one to conclude, incorrectly, that the inclusions are randomly oriented. © 2001 American Institute of Physics. [DOI: 10.1063/1.1363608]

I. INTRODUCTION

Studying assemblies of magnetic nanoparticles has become the daily bread of those concerned with the future of magnetic recording media. The theory of noninteracting assemblies is often used as a starting point for the interpretation of experimental data. It is particularly compelling for its simplicity, and is formally valid when the anisotropy energy of the particles is much larger than the magnetostatic interparticle interaction energy. Including magnetostatic effects complicates the theory due to the long range nature of the dipole–dipole interaction. Bertram and Bhatia¹ have used a mean field approach to show that magnetostatic interactions lead to a reduction of the remanent magnetization M_r . Also using mean field theory, Chantrell and Wohlfarth² have discussed the temperature dependent magnetic properties of assemblies of monodomain particles. While clearly recognized to be important when temperature effects are considered,³ interparticle interactions are often neglected in discussions of the quasi-static magnetic properties such as MH loops at zero temperature.⁴ This is because, for samples with isotropically distributed anisotropy axes, the theory of noninteracting particles describes the qualitative aspects of the MH loop rather well.

Recently, Honda *et al.*⁵ have shown that nanocomposites can be formed with magnetic particles that are crystallographically aligned. In this case the nanoparticles are single-crystal Fe cubes with mean edge size of 14 nm that are well

separated at a volume fraction of 10%. The particles are randomly distributed in the near surface region of a nonmagnetic single crystalline host material (yttrium-stabilized zirconia). Magnetically the samples can be considered as a film of randomly positioned but crystallographically aligned single-domain nanoparticles. Interestingly, the magnetic hysteresis of these samples does not show the anisotropy one would expect from noninteracting oriented cubic particles. Since the particles are embedded in a matrix, it is not entirely clear whether the effective anisotropy of the particles is really aligned with the cube edges. In the present article we show in a model calculation, that as a consequence of magnetostatic interactions, the magnetization curves will lack anisotropy, even if we assume that the easy axes are perfectly aligned.

II. THE MODEL

Our present task is to model a layer of Fe cubes that are crystallographically oriented but randomly distributed in space with given average size and volume fraction. We first choose the box dimensions L_x , L_y , and L_z ; initially only the aspect ratio is important (we have used 10:10:1) because we will later rescale all lengths. We then pick a set $\{\mathbf{r}_i\}$ of N points at random from the box, for particle centers. If we simply picked particle sizes at random, we would risk overlap of the particles—we want the largest particles to go in the largest holes. We accomplish this by defining $V_v(\mathbf{r}_i)$ to be the volume of a Voronoi polyhedron about point \mathbf{r}_i , and choosing the volume of the Fe cube centered at \mathbf{r}_i to be L_i^3

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$=fV_v(\mathbf{r}_i)$ where f is the desired volume fraction. To determine the overall length scale, we use our knowledge of the mean size \bar{L} , rescaling lengths so that $\sum_i L_i/N = \bar{L}$.

This construction leads to a normal distribution of the particle sizes. The exact shape of distribution is not crucial for the calculations presented here.

Magnetically, the particles are considered to be point dipoles with moments $m_i = M_s L_i^3$, where M_s is the saturation magnetization. The particles interact magnetostatically and have cubic anisotropy with easy axes aligned with the edges of the bounding box. This leads to the following magnetic energy:

$$E = - \sum_i \mathbf{H} \cdot \mathbf{m}_i + \sum_i K L_i^3 (\alpha_{ix}^2 \alpha_{iy}^2 + \alpha_{iy}^2 \alpha_{iz}^2 + \alpha_{iz}^2 \alpha_{ix}^2) + \frac{1}{2} \sum_{i \neq j} \frac{\mathbf{m}_i \mathbf{m}_j - 3(\mathbf{m}_i \mathbf{n}_{ij})(\mathbf{m}_j \mathbf{n}_{ij})}{|\mathbf{r}_i - \mathbf{r}_j|^3},$$

where \mathbf{H} is the applied field, $\alpha_i = \mathbf{m}_i/m_i$, and K is the anisotropy parameter, \mathbf{r}_i are the positions of the particles, and $\hat{\mathbf{n}}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/|\mathbf{r}_i - \mathbf{r}_j|$.

In the present work we will model the low temperature (4 K) hysteresis loops^{5,11} by calculating quasistatic magnetization curves as follows. We start with a random configuration of particle moments (demagnetized state) and integrate⁶ the Landau Lifshitz (LL) equation with no applied field and an arbitrary damping parameter $\alpha = 0.1$,⁷ until the moment directions stop changing. The applied field is then increased in discrete steps. At each step the LL equation is integrated using the initial condition from the output of the previous field step. When saturation is reached, a full hysteresis loop is then modeled using the same procedure with the field changing in small discrete steps.

III. RESULTS AND DISCUSSION

The Fe particles in the experimental sample⁵ have a magnetization that is equal to the bulk value and an effective anisotropy which is about 40% larger than the magnetocrystalline anisotropy of bulk Fe. We thus choose $M_s = 1745 \text{ emu/cm}^3$ and $K = 8.3 \times 10^5 \text{ erg/cm}^3$ in our calculations. We note, that the anisotropy parameter chosen here is considerably smaller than that observed by Chien³ in Fe in SiO₂ but comparable to the anisotropy measured by Bodker *et al.*⁸ for Fe particles on carbon support. For the present calculations we have used a sample of $N = 100$ particles in a box with aspect ratio $l_x:l_y:l_z = 10:10:1$ and open (nonperiodic) boundary condition. Calculations with larger numbers of particles using different numerical techniques to evaluate the long range dipole sums are currently under way. However, as we will see later, the relatively small sample size used here is sufficient to explain the qualitative properties of the zero temperature magnetization curves.

The quasistatic magnetization curves at zero temperatures calculated for $f = 1/8$, $f = 1/64$, and $f = 0$ (noninteracting particles) are shown in Figs. 1(a), 1(b), and 1(c), respectively. The curves shown in Figs. 1(a) and 1(b) represent ensemble-averages over ten samples.⁹ The noninteracting results in Fig. 1(c) are shown both as a test of the numerical

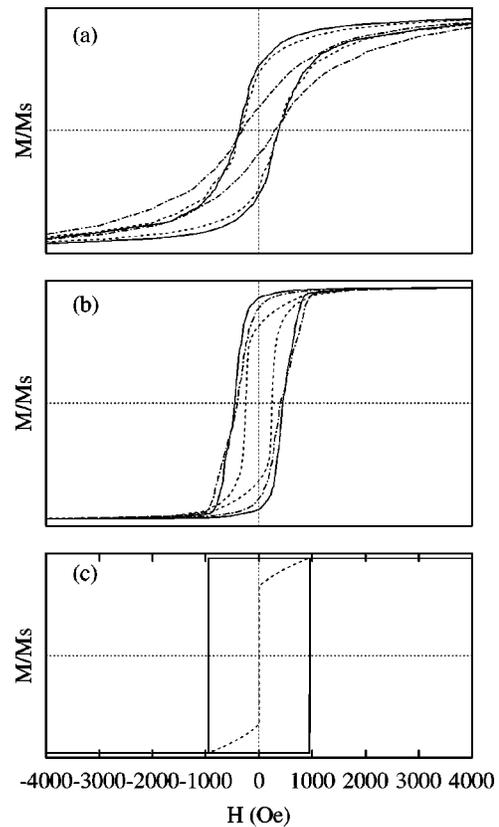


FIG. 1. Magnetization curves for assemblies of interacting Fe particles with volume fractions (a) $f = 1/8$ and (b) $f = 1/64$, as well as (c) for noninteracting particles. The external field was applied along the (100) (solid lines), (110) (dashed lines), and (001) (dashed-dotted line) directions, respectively.

procedure and as a reminder of what magnetic behavior should be expected when the particles do not interact. Since we have assumed a cubic anisotropy the loop is perfectly square with coercive field $H_c = 2K/M_s = 951 \text{ Oe}$ when the field is applied along the (100) direction of the cube. When the field is applied along the (110) direction, the remanence has to be $M_r/M_s = 1/\sqrt{2}$.

When we introduce interactions [Figs. 1(a) and 1(b)], three changes are conspicuous. (1) The discontinuity of the hysteresis loop at the coercivity, where the noninteracting particles fall over an energy barrier, is rounded. (2) The out-of-plane hysteresis loop narrows significantly, with lower remanence and coercivity. (3) The in-plane anisotropy [the difference between the solid and dashed curves in Fig. 1(a)] is much decreased. We will discuss these three changes later.

(1) In understanding the rounding of the hysteresis loop, the concept of ‘‘frustration’’ may be useful. We can see that random magnetostatic interactions can lead to frustration by considering a triangular configuration of particles, with the magnetization vectors perpendicular to the plane of the triangle. In this geometry the magnetostatic interaction is effectively antiferromagnetic; this can be accommodated in a ring with an even number of members, but in the case of a triangle there is frustration. This is known in the theory of spin glasses to lead to a very complex energy surface with many local minima.¹⁰ During magnetization reversal the system is forced from one local minimum to the next, which leads to a

gradual change of the magnetization as a function of the applied field and therefore to rounded loops.

(2) The narrowing of the out-of-plane loop can be understood as an effect of the shape anisotropy of the bounding box, which makes this a hard axis. (Note, however, that this shape anisotropy may be underestimated because of the small size of the system.)

(3) The decrease of in-plane anisotropy is more surprising, but agrees with the experimental results,⁵ in which coercivity is the same for both in-plane directions and the cubic anisotropy of the particles produces only a small anisotropy in the remanence. Reducing the volume fraction, Fig. 1(b), clearly begins to restore to the hysteresis loop the cubic anisotropy possessed by the particles. The suppression of in-plane anisotropy by interactions can be understood in terms of the relative size of these two effects, quantified by the ratio $\alpha \equiv 4\pi M_s^2 f / 2K$. For the parameters used in our calculations α takes the respective values of 2.9 ($f=1/8$) and 0.36 ($f=1/64$). That is, for $f=1/8$ the magnetostatic interactions dominate, while for $f=1/64$ the anisotropy energy is more important.

Two additional changes in the hysteresis result from the magnetostatic interactions. The saturation field is increased significantly, while the coercivity is reduced from 951 Oe in the noninteracting case to 350 Oe in the case of $f=1/8$. The former effect can be understood because interactions with randomly placed neighbors force the particle moments to be noncollinear, so they are harder to align: the saturation field is higher. This is consistent with experiment,¹¹ in which the measured saturation field is much larger than what would be expected from the measured coercivity if the particles are assumed to be noninteracting. The reduction in coercivity may be understood in terms of demagnetization by effective antiferromagnetic interactions.

Qualitatively, the changes in the hysteresis loop that result from the magnetostatic interactions seem similar to those that result from random orientations of the anisotropy axes. In both cases the hysteresis loop appears isotropic and the remanence seems to be reduced. While this leads to the temptation to ignore magnetostatic interactions between Fe particles, the present calculations for crystallographically oriented Fe cubes show that the magnetization reversal is qualitatively different when interactions become important. In the noninteracting case the reversal is coherent and the hysteretic losses are due the crossing of a single energy barrier. In the

interacting case, the reversal is inhomogeneous and the hysteretic losses are due to a sequence of energy barriers that have to be crossed and thus give rise to a rounded magnetization curve. This qualitative difference in reversal mechanisms will affect the dynamics and leads to the conclusion that long range magnetostatic interactions must be included when the dynamics of reversal is investigated at finite temperatures.

IV. SUMMARY

We have simulated an array of crystallographically oriented iron particles, including magnetostatic interactions. We find that magnetostatic interactions cause qualitative changes in the hysteresis curves, and hence, cannot be ignored in modeling these systems.

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⁶Throughout this work we use a fourth order Runge Kutta algorithm with fifth order error estimates and adapt the time step during the integrations such that the error is always less than 10^{-14} .

⁷Note that in the present calculations, the damped LL equation is merely used to find the local energy minimum.

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⁹The hysteresis curve for each of the ten samples looks much like the ensemble average, but is somewhat more noisy. The ensemble average is a better approximation to a real nanocomposite with a much larger number of particles.

¹⁰It should be noted that this argument is most valid for short ranged interactions—it is possible that the long range of dipolar interactions may wash out the frustration effect.

¹¹K. D. Sorge *et al.* (these proceedings).