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Nonmonotonic concentration dependence of magnetic response in Fe nanoparticle-polymer composites

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We report the magnetic response of composites formed by dispersing Fe nanoparticles in a polymer. Transmission electron microscopy reveals the formation of chain-like entities of nanoparticles. The magnetic response (hysteresis, remanence ratio, exchange bias, etc.) is in general nonmonotonic as a function of the particle concentration in the composites. The coercivity and remanence go through a maximum, while the exchange bias and magnetic relaxation rates go through a minimum, with increasing concentration. The effects are interpreted as being a consequence of a competition between an increasing anisotropy due to the formation of the chain-like entities that tends to increase the remanence, etc., and the weakening of these effects at higher concentrations due to the interactions between these entities.

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I. INTRODUCTION

The effects of interparticle interactions for assemblies of magnetic nanoparticles have become the subject of great interest in recent years. Both the dipolar and exchange interactions can occur between nanoparticles depending on the interparticle distances and agglomeration. The dominant interactions in dispersed magnetic nanoparticle assemblies in insulating matrices are dipolar interactions,[1] while exchange interactions may occur for systems where particles are in contact. There have been many studies concerning the simulation of these interactions, but there have been relatively few experimental reports. In real systems, due to distributions in particle size, particle clustering, and random magnetization orientations, results on these interactions have been conflicting. For example, several researchers have reported an increase in the blocking temperature T_B, as a result of dipolar interaction, with increases in nanoparticle concentration,[2–4] while others have reported a decrease in T_B with particle concentration.[5] Similarly, the remanence for interacting particle systems had been found to decrease by some researchers,[6,7] while it was found to increase by others.[8] Special interest has come to focus on the variation of interparticle effects in magnetic nanoparticle and polymer composites due to their potential applications. A variety of results on the coercivity variation in polymer composites have been reported that describe independent, decreasing, and nonmonotonic trends with concentration.[9–11] A variety of results on the effects of self-aggregation and chaining of the nanoparticles[12] have also been reported in the composites' assemblies. In view of the lack of clarity on the effects of interparticle interactions on the coercivity, remanence, magnetic relaxation, exchange bias, etc., and the relative importance of the self-aggregation effects in such assemblies, it appears useful to study the response of nanoparticle polymer composites with varying particle concentrations coupled with a microstructural analysis to correlate the structural and magnetic features.

The goal of this work was to investigate particle interactions for Fe-oxide passivated Fe nanoparticles. Particle interaction effects were investigated by dispersing the particles in a polymer, polymethylmethacrylate (PMMA), at different concentrations. These concentrations were compared to the case of the same sample of pure Fe-oxide passivated Fe nanoparticles pressed into a pellet. The interaction effects are shown to lead to a nonmonotonic variation of most of the magnetic response including the coercivity, remanence, magnetic relaxation, and the exchange bias effects. These features are explained in terms of competing tendencies of the interparticle dipolar interactions and chaining effects between the nanoparticles.

II. EXPERIMENT

All of the Fe nanoparticles studied in this work were prepared by an inert gas condensation (IGC) technique.[13] To form Fe/PMMA nanocomposites, Fe nanoparticles were dispersed by sonication into a solution of PMMA polymer and

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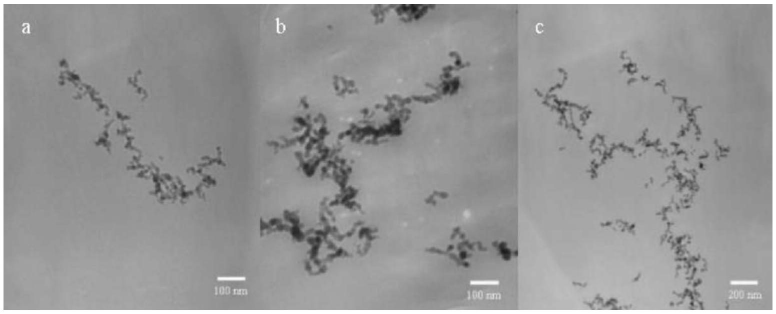

FIG. 1. Cross-sectional TEM images of 0.5 mg (a), 1.5 mg (b), and 4 mg (c) samples showing a single chain-like entity (a), clustering of chain-like entities (b), and tendency of branching on chain-like entities (c).

acetone. Typically, there is an optimal power for sonication. A high power sonication tends to cause reagglomeration. Therefore, the sonication processes were performed close to the optimum power and for short time intervals in order to avoid reagglomeration. The solution was then spin cast until it hardened into a thick film. The particles were dispersed in five concentrations of 4.0, 3.0, 1.5, 1.0, and 0.5 mg of Fe in 100 mg of PMMA polymer. Characterization of the nanocomposites was carried out with transmission electron microscopy (TEM), and x-ray diffraction (XRD). Magnetic measurements were carried out in a dc extraction magnetometer, using a Physical Properties Measurement System (PPMS) apparatus by Quantum Design Corporation.

III. RESULTS AND DISCUSSIONS

A. Structural and magnetic properties

Figures 1(a)–1(c) show cross-sectional TEM images of Fe/PMMA nanocomposite samples with 0.5, 1.5, and 4.0 mg Fe nanoparticles in 100 mg PMMA polymer. In the images, the particles are found to occur in small agglomerates and chains separated by distances of several hundred nanometers. The lengths of the chains themselves vary between 70 and 400 nm. With increasing concentration of the Fe particles in the composite, the concentration of the chains appears to increase as does the tendency to form side branches. The particle size distribution obtained using Figs. 1(a)–1(c) is given in Fig. 2. The distribution has a narrow width of about 2 nm. The particle size obtained from x-ray diffraction using Scherer's formula is about 10.8±0.5 nm. The average particle size obtained from logarithm-normal fit to Fig. 2 is about 14.5±0.5 nm, which suggests that the shell size is about 2 nm.

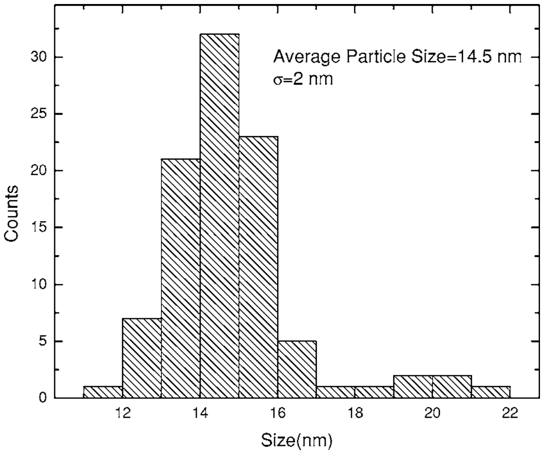

FIG. 2. Particle size distribution obtained by using 100 particles.

The magnetic measurements were performed with a commercial Quantum Design PPMS. The hysteresis measurements referred to as "field cooled" were performed after the samples had been cooled to the lowest temperature in the indicated field. Field-cooled (FC) magnetization measurements were taken during the cool down in the field. Zero-field-cooled (ZFC) measurements were performed in the indicated field after cooling down in the zero field.

The magnetic characteristics of the particles used to form the composites have been described in detail elsewhere.[13,14] The particles have a core and/or shell structure, are ferromagnetic at room temperature, and, as compressed pellets, have a coercivity of ~500 Oe. Their coercivity increases to ~1500 Oe at 5 K and significant exchange bias effects[15] are observed below ~65 K. These exchange bias effects that are manifested in a shifting of the hysteresis loops in the direction opposite to that of the cooling field have been understood as being due to the interaction of the ferromagnetic Fe core with the ferrimagnetic Fe-oxide shell. The blocking temperature T_B, defined as the temperature where the ZFC and FC magnetization curves separate, obviously decreases with increasing field, e.g., T_B is ~102 K at 5000 Oe and is ~55 K at 2 T. Low field ac susceptibility measurements suggest a rapid growth of the anisotropy below ~80 K.[14] This temperature (80 K) corresponds to the temperature below which the exchange bias effects in these particles become significant.

As discussed earlier, five different concentrations of the nanoparticle composites were studied and compared to the pelletized sample. The zero-field-cooled coercivity of the samples was measured at various temperatures, in particular at 5 K and room temperature. The variation of the coercivities for the different Fe concentrations at 300 K are shown in Fig. 3, where we also show the value for the compressed pellet for comparison. It is clear that the coercivity goes through a maximum as a function of the concentration, peaking at around 1.5 mg. The value of the coercivity reaches a maximum of about 900 Oe that is *almost twice* the value for the compressed pellet. It is also apparent that the values for the highest concentrations, 4.0 mg, though still above the value for the compressed pellet begin to decrease toward it systematically. The temperature dependence of the coercivities of the composites and the pellet are shown in Fig. 4. It is

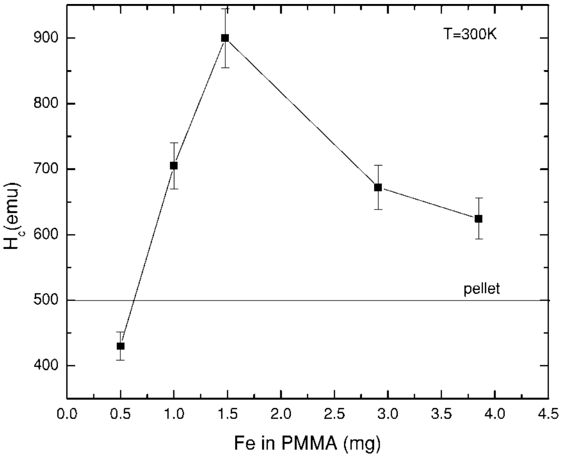

FIG. 3. Coercivity at 300 K for different compositions showing a clear peak and an approach toward the value of the pelletized sample at highest concentrations.

clear that the nonmonotonic trend is present independent of temperature and it is most apparent at the room temperature. As we have reported earlier,[13] larger size Fe nanoparticles (~16 nm) show room temperature coercivities (~800 Oe) that are comparable to the values observed in these high concentration composites.

In addition to the coercivity, simulations have also shown the variation of the remanent moment ratio (Mr/Ms) with increasing particle concentration.[1,16,17] In general, the dipolar interactions tend to lower the remanence by creating flux closure loops while the exchange between the nanoparticles tends to increase the remanence by creating larger coupled units, typically up to a maximum. We have also determined the variation of this parameter for the composites and the compressed pellet. Determination of the room temperature value of the remanence ratio for the composites is made difficult, particularly at low concentrations, due to the large diamagnetic background at high fields. However, within the limitations of the data, it does appear that a broad maximum is developed in the remanence ratio with high concentration values clearly converging toward the remanence ratio of the compressed pellet, $Mr/Ms \sim 0.35$, from a maximum of ~0.51 at intermediate concentrations. At the lowest temperature (5 K) while the variation in Mr/Ms with concentration is relatively small, a peak is very clearly evident at the same concentration where the coercivity shows a maximum (Fig. 5). The maximum value of 0.51 is in agreement with the value expected for a system of particles with uniaxial anisotropy, while the reduced values in the neighborhood of this maximum are suggestive of the effects of dipolar interparticle interactions.

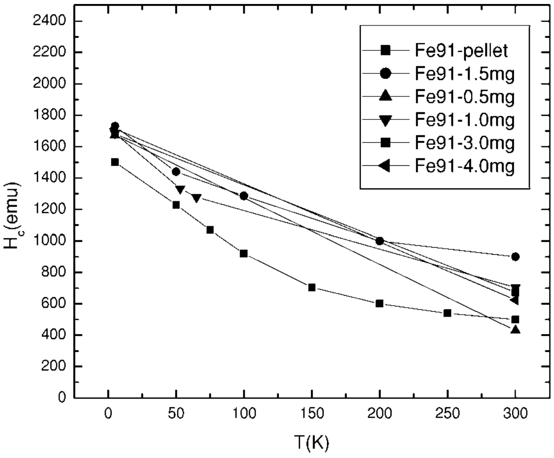

FIG. 4. Coercivity as a function of temperature for different compositions.

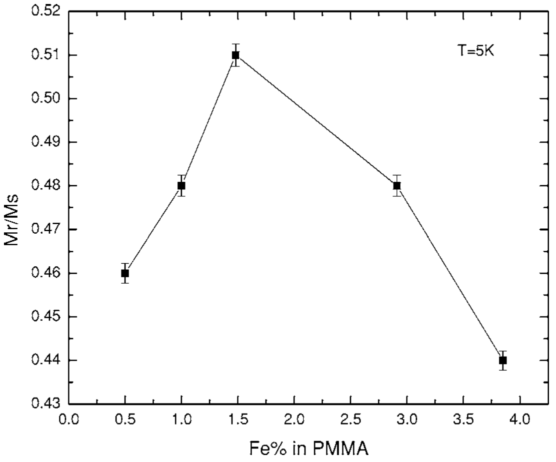

FIG. 5. Remanence ratio as a function of composition at 5 K. Peak is evident.

It is worth pointing out that in the pelletized form the remanence ratio for these particles rises from 0.35 at room temperature to 0.5 at ~80 K, indicating the domination of a *uniaxial* anisotropy, most probably due to the interaction of the core moments with the oxide shell. The lowered values at room temperature suggest the degradation of uniaxial anisotropy, at least partly, due to the effects of the randomizing dipolar fields. However, we note that the temperature (80 K) where the remanence ratio of the pellet reaches ~0.5 is close to where the exchange bias in these particles becomes nonzero, suggesting a correlation between the two effects. The large coercivities (~1500 Oe) in Fe nanoparticles at low temperatures have typically been attributed to the effects of the surface anisotropy and to the effects of the exchange anisotropy originating from the (Fe) core and oxide shell interaction. The latter is also understood to be the source for the shifting of field-cooled hysteresis loops, the so-called *exchange bias*. While we have not come across any studies on the effects of interparticle interactions on the exchange bias, it seems reasonable to assume that *interparticle* dipolar and exchange fields that compete with the *intraparticle* anisotropy to affect the coercivity and remanence, as discussed above, may also affect the blocking of the moment along the direction of the unidirectional anisotropy that characterizes the exchange bias. Our measurements of the exchange bias in the nanocomposites were performed by field cooling the materials in a field of 2 T from 300 K. Shifted hysteresis loops were obtained as in the case of the compressed pellet. The exchange bias H_{EB} was determined from these loops as equal to half the difference between the coercivities in the negative and positive direction, $H_{EB}=(H_C^- - H_C^+)/2$.

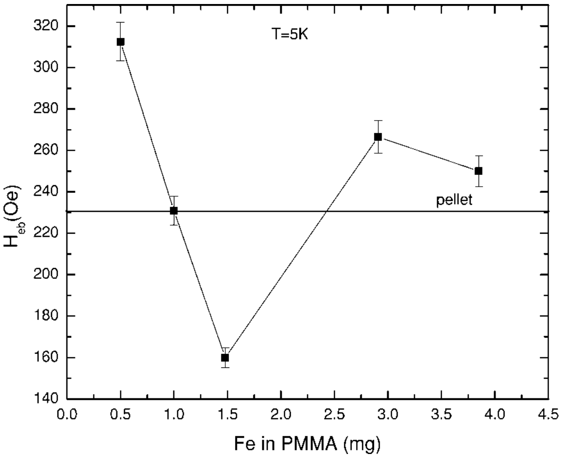

FIG. 6. Magnitude of the exchange bias at 5 K in 2 T cooling field for different compositions. Minimum is evident at the same composition where a maximum is observed in the coercivity and remanence.

The data for the pellet and the composites at 5 K are shown in Fig. 6. At the lowest concentration, the exchange bias was observed to increase considerably, by about 33%, compared to the value for the pellet, but then goes through a minimum at the same concentration (1.5 mg) where the coercivity and remanence were observed to peak. The decrease in the exchange bias at the minimum is quite substantial, being about 50% of the low concentration value. At the highest concentrations, we again find the exchange bias values approaching the value observed for the pellet. Thus, our data suggest that interparticle interactions affect the coercivity (remanence) and exchange bias in opposite ways, with the most isolated particles showing the highest exchange bias and subsequently as particles interact and most probably form larger coupled units, the exchange bias is very significantly reduced. However, for both the coercivity and the exchange bias, the values ultimately tend toward the high concentration limit defined by the pelletized sample. This nonmonotonic trend for the exchange bias as a function of the concentration, as in the case of the coercivity and the remanence, again suggests that the interparticle effects have a maximum effect in an intermediate range of compositions.

In view of the fact that both the coercivity and the remanence show a pronounced trend with concentration, it is reasonable to expect that this would also be reflected in the thermal stability of the moment since the coercivity in nanoparticle systems is dependent to a large extent on the thermal excitation of moments over anisotropy barriers. Increased coercivity, in this view, should be indicative of lowered magnetic relaxation. We find that this is indeed the case, and the magnetic stability of the moments undergoes a very pronounced increase in the same concentration range where the coercivity and remanence show a maximum. The magnetic relaxation was conducted by field cooling the composite samples in a field of 5000 Oe that was rapidly reduced to zero after being on for approximately 600 sec. The ensuing changes in the moment were recorded for at least 2400 seconds. As is typical for magnetic particles with a finite size distribution and relaxation in a limited time window, the data were fit to a logarithm function,[16]

$$M(t) = m_o[1 - Sln(1 + t/\tau)],$$

where S is the rate of relaxation. Typically the rate parameter S is found to be inversely proportional to the magnitude of the anisotropy energy barriers separating the easy axes of the nanoparticle moments.

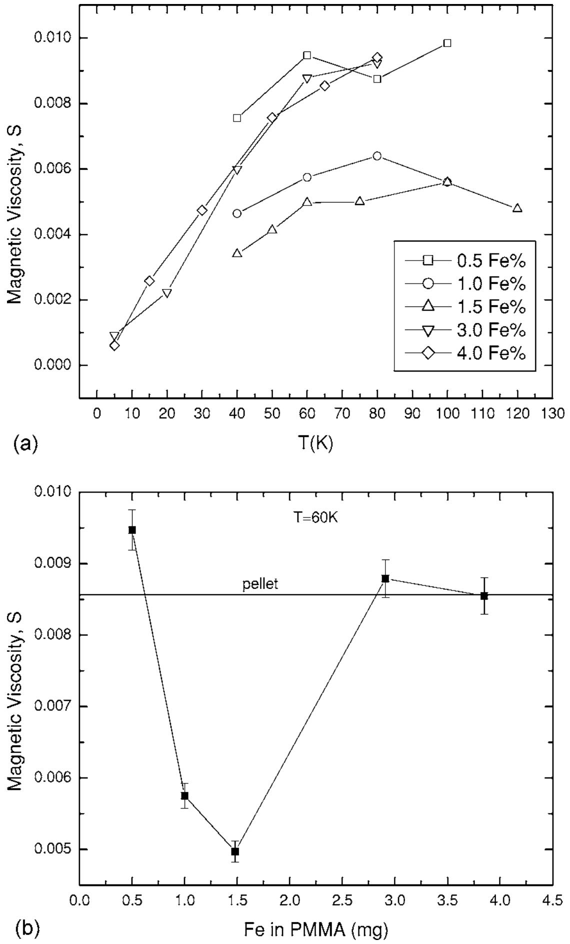

FIG. 7. Temperature dependence of the relaxation rate S for different composites showing a maximum typically around 80 K (a). Relaxation rate at 60 K for different composition showing a minimum at the same composition where the coercivity is a maximum and the exchanges bias is a minimum (b).

The relaxation was studied at different temperatures for the various concentrations and the variations are shown in Fig. 7(a), while in Fig. 7(b), we show the rate of relaxation at 60 K as a function of the concentration. The temperature dependence of the rate for the different concentrations typically shows a peak between 80 and 100 K while the maximum value of the rate depends systematically on the concentration. This latter trend is clear from Fig. 7(b), where a pronounced minimum in the rate S is apparent for the same concentrations where the coercivity and remanence have a maximum. It is evident that increasing the concentration again affects the relaxation rate in a nonmonotonic way with the very low concentrations having a higher relaxation rate and at intermediate concentrations, there is a very pronounced degree of thermal stability of the remnant moment. This in turn suggests the growth with increasing concentrations of the effective energy barriers preventing the randomization of the moments until at very high concentrations, the relaxation rates again rise toward those of the compressed pellet.

For very low temperatures ($T < 20$ K), the decrease in the relaxation rate compared to the palletized sample was very stark and the moment undergoes virtually no relaxation for the entire period of our measurement (2400 sec), for the concentrations $x < 0.5$ mg. There is a slight increase in the relaxation with increasing concentration in this low temperature range with the 3 mg sample showing a very small but measurable relaxation at 20 K and the 4 wt. % and the palletized sample showing relaxation at all temperatures. Hence, it is apparent that at very low temperatures, the effect of increasing concentration is a monotonic increase of the relaxation rate. This is in contrast to the behavior at higher temperatures ($T > 50$ K) discussed above, where we see a nonmonotonic change with the concentration. The very pronounced decrease in the relaxation rate, at low concentrations suggests the development of a large effective anisotropy barrier that inhibits the relaxation until about 30–40 K for most concentrations. With increasing concentration the interparticle interactions appear to diminish these effects.

B. Discussion

As discussed previously, the TEM results clearly indicate the formation of chain-like structures of nanoparticles of varying lengths. These chain-like structures grow more numerous with increasing concentration and it is reasonable to assume that the overlapping of these structures and their mutual interactions would also grow as the distance between them decreases. We understand that the concentration dependence of the effects we have described arise from these microstructural changes. It appears from a comparison of the coercivity, relaxation, and exchange bias data that the effects of increasing concentration have a twofold character. First, there is the development of a uniaxial type anisotropy most probably associated with the chaining of nanoparticles that tends to stabilize the remanence and increase the coercivity. Second, there is the development of interparticle interactions that tend to randomize the moments and degrade the remanence. At the lowest temperature, as far as the exchange bias and thermal stability are concerned, the most dilute composition (0.5 wt. %) appears to gain from both of the above factors. The smallness of the interparticle dipolar effects and the relative absence of the agglomeration effects enhance both the exchange bias and the stability of the moment. However the coercivity is low most probably due to the relative smallness of the size dependent anisotropy originating in the chaining of the nanoparticles. At the lowest temperatures, as the concentration is increased and the interparticle effects increase, the exchange bias and thermal stability decrease, while the chaining effects enhance the coercivity and remanence for the same compositions. With an increase in temperature ($T > 40$ K), the growth of anisotropy due to chaining appears to predominate with more concentrated compositions actually showing not only a larger coercivity and remanence but also enhanced stability of the moments compared to the lower concentrations. The decrease in the exchange bias with concentration is consistent both with the increase of interparticle dipolar forces and the growth of the uniaxial anisotropy of the chain-like structures. We believe that both these developments weaken the net effects of the *intraparticle* exchange anisotropy. It is suggested that the (shape) anisotropy induced by the chaining tends to compete with the exchange anisotropy in blocking the moment leading to lowered exchange bias.

We now come to the curious part of the observed trends that is the observation of a *peak* in most of the properties as a function of concentration. Some researchers have indeed observed similar behavior in experimental results. Bottoni and co-workers[17] showed that the coercivity increases with packing fraction, peaks, and subsequently decreases for acicular Fe nanoparticles. They observed that the increase was due to the formation of chains of particles as the packing fraction increases, which behave as a single particle having a large shape anisotropy. Other researchers have observed increases in coercivity with magnetic nanoparticle loading in polymers[18] and agglomeration in polymers,[19] as well as peaks in coercivity behavior.[10,20]

To explain this nonmonotonic trend in our system, we note that while some simulations have indeed reported the observation of a peak in the coercivity and remanence,[1,21,22] most of the simulations, over most of the ranges of dipolar energy, exchange energy, anisotropy, and temperature show a monotonic decrease with increasing concentration. In the few cases where simulations have shown a peak, it is invariably for the cases where the isolated particles ($c = 0$) are small enough to be *superparamagnetic* at the given temperature of the simulations. With increasing concentration, the dipolar interactions initially create a residual field with which the moments of the nanoparticles lock onto giving a nonzero coercivity and remanence. As demonstrated by Mørup and Tronc,[5] blocking of the superparamagnetic moments takes place when the dipolar energy becomes comparable to the thermal energy. At higher concentrations, the interactions become more long range producing flux closure configurations which decrease the coercivity for blocked particles. However, as pointed out by Verdes and co-workers,[21] the crucial parameter for the observation of a peak effect is the ratio of the parameter KV/kT with a peak effect being confined to systems where this parameter is small viz. a weakly interacting system with small anisotropy energy as compared to the thermal energy. It is unlikely, however, that this is the explanation for the observed peak effect in our particles that are *blocked* and have very significant coercivity even at room temperature. At even lower temperatures, the coercivity and by implication, the anisotropy, is very large and the small KV/kT criteria does not appear to hold and the average particle behavior is not even close to being superparamagnetic. It is possible that given a particle size distribution in our samples, we may have a small number of superparamagnetic particles that block due to interparticle effects and lead to an increase in average coercivity. However, it appears very unlikely that the blocking of a small number of these particles can lead to a *doubling* of the average coercivity, as we observe, at room temperature. The main difference between the experimental situation and the simulations is that in a real system a systematic decrease in particle-particle separation upon increases in packing may not be easily realized but agglomeration and coalescence effects have to be taken into account as well. This tendency is manifest in our work where nanoparticles form small chains and clusters, as is evident in the micrographs in the Figs. 1(a)–1(c). As more particles are added to the composite, the chains and clusters increase in size. Within the small clusters or chains, dipolar interactions may be present, and the dipolar interaction increases as the clusters grow. Thus, an increase in dipolar strength is occurring, causing increases in energy barrier height. For low concentrations, the clusters may be considered as separated too much for dipolar interactions between the clusters to be effective, as the interaction decreases with $1/d^3$, where d is the particle separation, except at a percolation threshold. Similar results were obtained in a modeling study by Kechrakos and Trohidou.[1,22] They found that for a purely dipolar system (zero anisotropy energy), a peak in coercivity occurs for particle packing when "fractal"-like clusters appear with chain-like branches. The arrangement leads to "nose to tail ordering" of their moments and an enhanced magnetization. Further increases in concentration reduce the fractal morphology until a fully periodic system occurs. Incorporating the effects of both exchange and dipolar forces they found[22] that a peak structure in the coercivity is again observed. We suggest that in our system the basic mechanism is similar to this viz. the growth of the chain-like entities formed by exchange and dipolar interactions between particles and the development of anisotropy, most likely shape anisotropy, associated with the formation of these magnetic entities. This anisotropy results in enhanced coercivity and thermal stability, etc. With increasing concentration, however, the interactions *between* the chains weaken the effects of this anisotropy, in a similar fashion to the simulations. On the other hand, it appears that exchange bias effects are significantly diminished due to interparticle effects, an observation that requires more experimental and theoretical follow up. Finally, we note that our study utilized composites containing relatively larger nanoparticles that are blocked at room temperature. We are extending the current work to consider the interparticle effects in composites formed from smaller nanoparticles that are superparamagnetic at room temperature to determine the effects of interparticle interactions in this context.

To obtain more insight in real situations, our work suggests the need for more complex simulations of magnetic particle dispersions in composites where the effects of increasing concentrations may include the development of dipole and exchange interaction mediated chaining and the consequent growth of anisotropy.

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[1] D. Kechrakos and K. N. Trohidou, Phys. Rev. B **58**, 12169 (1998).

[2] J. L. Dorman, L. Bessais, and D. Fiorani, J. Phys. C **21**, 2015 (1988).

[3] S. Gangopadhyay, G. C. Hadjipanayis, C. M. Sorenson, and K. J. Klabunde, IEEE Trans. Magn. **29**, 2619 (1993).

[4] R. W. Chantrell, M. El-Hilo, and K. O'Grady, IEEE Trans. Magn. **27**, 3570 (1991).

[5] S. Mørup and E. Tronc, Phys. Rev. Lett. **72**, 3278 (1994).

[6] W. Luo, S. R. Nagel, T. F. Rosenbaum, and R. E. Rosensweig, Phys. Rev. Lett. **67**, 2721 (1991).

[7] R. W. Chantrell, in *Magnetic Hysteresis in Novel Magnetic Materials*, edited by G. C. Hadjipanayis, NATO Advanced Study Institute, Series E, Applied Sciences (Kluwer, Dordrecht, 1997), Vol. 338, p. 21.

[8] S. Mørup, F. Bodker, P. V. Hendriksen, and S. Linderoth, Phys. Rev. B **52**, 287 (1995).

[9] J. L. Wilson, P. Poddar, N. A. Frey, and H. Srikanth, J. Appl. Phys. **95**, 1439 (2004).

[10] J. J. Blackwell, M. P. Morales, K. O'Grady, J. M. González, F. Cebollada, and M. Alonso-Sañudo, J. Magn. Magn. Mater. **242–245**, 1103 (2002).

[11] E. Tronc, D. Fiorani, M. Noguès, A. M. Testa, F. Lucari, F. D'Orazio, J. M. Grenèche, W. Wernsdorfer, N. Galvez, C. Chanéac, D. Mailly, and J. P. Jolivet, J. Magn. Magn. Mater. **262**, 6 (2003).

[12] M. Vazquez, C. Luna, M. P. Morales, R. Sanz, C. J. Serna, and C. Mijangos, Physica B **354**, 71 (2004); A. A. Novakova, V. Yu. Lanchinskaya, A. V. Volkov, T. S. Gendler, T. Yu. Kiseleva, M. A. Moskvina, and S. B. Zezin, J. Magn. Magn. Mater. **258–259**, 354 (2003); S. Anders, M. F. Toney, T. Thomson, J. U. Thiele, B. D. Terris, Shouheng Sun, and C. B. Murray, J. Appl. Phys. **93**, 7343 (2003); A. M. Testa, S. Foglia, L. Suber, D. Fiorani, L. Casas, A. Roig, E. Molins, J. M. Grenèche, and J. Tejada, *ibid.* **90**, 1534 (2001).

[13] C. Baker, S. Ismat Shah, and S. K. Hasanain, J. Magn. Magn. Mater. **280**, 412 (2004).

[14] C. Baker, S. K. Hasanain, and S. Ismat Shah, J. Appl. Phys. **96**, 6657 (2004).

[15] W. H. Meiklejohn and C. P. Bean, Phys. Rev. **102**, 1413 (1956); **105**, 904 (1957); A. E. Berkowitz and K. Takano, J. Magn. Magn. Mater. **200**, 552 (1999).

[16] R. Skomski and J. M. D. Coey, *Permanent Magnetism* (IOP Publishing, London, 1999).

[17] G. Bottoni, D. Candolfo, M. Cecchetti, A. R. Corradi, and F. Masoli, J. Magn. Magn. Mater. **120**, 167 (1993).

[18] J. Deng, X. Ding, W. Zhang, Y. Peng, J. Wang, X. Long, P. Li,

and A. S. C. Chan, Polymer **43**, 2179 (2002).

[19] S. Anders, M. F. Toney, T. Thomson, J-U. Thiele, B. D. Terris, S. Shouheng, and C. B. Murray, J. Appl. Phys. **93**, 7343 (2003).

[20] C. L. Chien, J. Appl. Phys. **69**, 5267 (1991).

[21] C. Verdes, B. Ruiz-Diaz, S. M. Thompson, R. W. Chantrell, and A. Stancu, Phys. Rev. B **65**, 174417 (2002).

[22] D. Kechrakos and K. N. Trohidou, J. Magn. Magn. Mater. **262**, 107 (2003).