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Experimental study of ferromagnetic chains composed of nanosize Fe spheres

L. Zhang and A. Manthiram*
Center for Materials Science & Engineering, ETC 9.104, The University of Texas at Austin, Austin, Texas 78712

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Chains composed of nanometer size spheres of Fe have been synthesized by a controlled reduction at ambient temperature of aqueous Fe^{2+} with KBH_4 in the presence of an applied magnetic field. The chains are characterized by x-ray diffraction, transmission electron microscopy, and superconducting quantum interference device magnetometry. The size of the crystalline Fe spheres could be varied from 20 to 70 nm by controlling the synthesis conditions. The magnetization reversal behavior of these chains are examined and compared with the theoretical predictions of the ''chain of spheres model.'' The observed values of the coercive force H_c, variation of H_c with particle size, relationship between the H_c values of randomly oriented and aligned chains, remanence of randomly oriented chains, and angular dependence of H_c in the single-domain region are all in support of a symmetric fanning mechanism for magnetization reversal. This study represents an example of fabrication of a true chain of spheres and comparison of their magnetic properties with theoretical predictions available in the literature. [S0163-1829(96)08729-2]

I. INTRODUCTION

The coercive force H_c of single-domain particles with shape anisotropy is much lower than that predicted by the classical modes of coherent rotation, curling or buckling. In order to explain the difference, Jacobs and Bean[1] introduced the chain of spheres model for magnetization reversal. In the chain of spheres model, elongated fine-particle magnets are considered to be composed of a linear chain of n single-domain spherical particles. Considering only magnetostatic interactions among the spheres without any exchange interactions, magnetization reversal in an applied field was assumed to proceed by a fanning mechanism. The fanning mechanism is shown schematically in Fig. 1 and compared with other classical modes. The chain of spheres model has been used commonly to explain the magnetization reversal in acicular particles of, for example, γ-Fe_2O_3 and Fe.[2,3] However, the acicular particles are not composed of a true chain of single-domain spheres. It would be of interest if materials with true chain of spheres could be made in the laboratory and also to examine their magnetization reversal behavior.

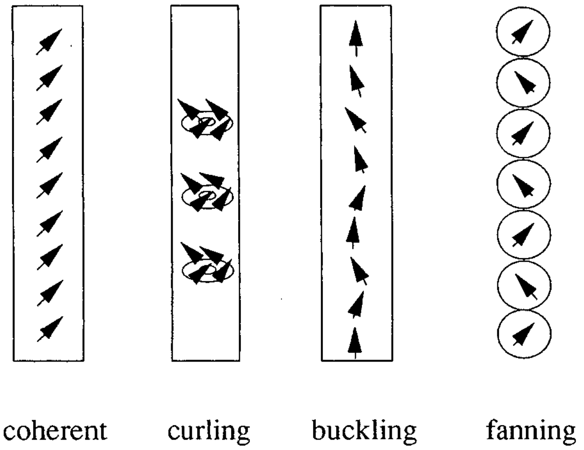

FIG. 1. Schematic representation of different modes of magnetization reversal.

Furthermore, the assemblies of chains of single-domain spheres can provide some attractive features from a practical point of view.[4] For example, H_c scales with the saturation magnetization M_s in the chain of spheres model, which can permit a satisfactory temperature dependence for H_c. The chains of spheres can be dispersed in a polymer matrix and oriented parallel or perpendicular to the film surface before curing the matrix, which will be of interest for longitudinal or perpendicular recording. It is much easier to achieve smooth film surface with the chains composed of spheres than with acicular particles.

However, preparation of chains composed of single-domain spheres of metals without introducing any passivating oxidized layers in between the spheres is difficult with existing technologies. Introduction of passivating layers is undesirable as they will reduce the important magnetostatic interactions. Oppegard, Darnell, and Miller,[5] showed 35 years ago that chains of single-domain Fe or Fe-Co alloy particles can be prepared by a reduction of aqueous Fe^{2+} or a mixture of Fe^{2+} and Co^{2+} with sodium borohydride. However, H_c was found to be around 600 Oe for Fe particles, which is much lower than the values predicted by the chain of spheres model of Jacobs and Bean.[1] Also, no attempt or detailed study was made to verify the mechanism for magnetization reversal. We describe here a controlled chemical reduction procedure employing aqueous alkali metal borohydrides to obtain chains composed of spherical Fe particles. A fast particle nucleation/growth on the adjacent spherical particles suppresses oxidation in between the spheres and ensures magnetostatic interactions. The observed magnetic properties of the chains are carefully examined and compared with the predictions of the chain of spheres model.

II. EXPERIMENTAL

Chains composed of spherical Fe particles were obtained by a two-step process involving first a controlled reduction of Fe^{2+} with potassium borohydride and then a subsequent heat treatment. Since the borohydride reduction is a fast exothermic reaction, it was performed in a T-form reactor in order to achieve a homogeneous composition and size distribution. The reaction was controlled carefully to allow the growth of particle chains and suppress self-nucleated particles by mixing specific concentrations of ferrous salt and borohydride. Equal volumes of aqueous solutions of 0.1 M $FeCl_2 \cdot 4H_2O$ and 0.5 M KBH_4 were allowed to mix in the T-form reactor in the presence of an applied magnetic field of 1500 Oe. The magnetic field was used to achieve the growth in one direction. Although the previous studies of borohydride reduction[5–7] lack the control of particle size, we found that the particle size can be controlled and varied within the desired nanometer range by the addition of varying amounts of ethanol to the aqueous solutions. The Fe particle chains so obtained was filtered, washed first with water and then with acetone, and allowed to dry overnight in a glove box filled with nitrogen. The samples were then heated in a furnace in a flowing 90% Ar–10% H_2 gas mixture first at 150 °C for 30 min to remove the moisture, and then at 500 °C for 1 h to clean the oxidized surface and to achieve better crystallinity of the particles.

The magnetic measurements were carried out with a superconducting quantum interference device magnetometer at 298 K. In order to compare the experimental results with the chain of spheres model, random and oriented particle chains were dispersed in a polyurethane film matrix and cured in the presence and absence of an applied magnetic field of 1500 Oe. As the polyurethane matrix, the plastic substrate, and the drinking straw used to hold the sample during the magnetic measurements produce a significant diamagnetic moment at higher fields, the observed magnetizations were corrected for this diamagnetic background. The data presented are all after this correction. The samples were also characterized by x-ray diffraction and transmission electron microscopy (TEM) equipped with an energy dispersive spectroscopic analysis. A high-resolution TEM with a beam point resolution of <1 nm was employed to study the crystal orientation of each particle in the chain. The boron contents in the samples were obtained by inductively coupled plasma analysis (ICPA).

III. RESULTS AND DISCUSSION

A. X-ray and microscopic characterization

X-ray powder diffraction recorded with the randomly oriented chains shows reflections corresponding to crystalline Fe having the bcc structure. The TEM photograph and electron diffraction recorded with randomly oriented chains are shown in Fig. 2. The photograph shows that the chains are composed of spherical Fe particles with a clear interface between the particles. The interface is more or less perpendicular to the chain growth direction. As the borohydride-reduction process is a fast exothermic process, we believe the interface between the spheres is free from oxidized layers, which assures magnetostatic interactions between the adjacent particles. Also, the spherical particles in the chains are found to be uniform in size with a variation of about ±3 nm. The electron-diffraction pattern recorded in a selected area shows polycrystalline bcc Fe, which is consistent with the x-ray data. High-resolution TEM with a convergent beam of <1 nm indicates that each spherical particle in the chain is a single crystal.

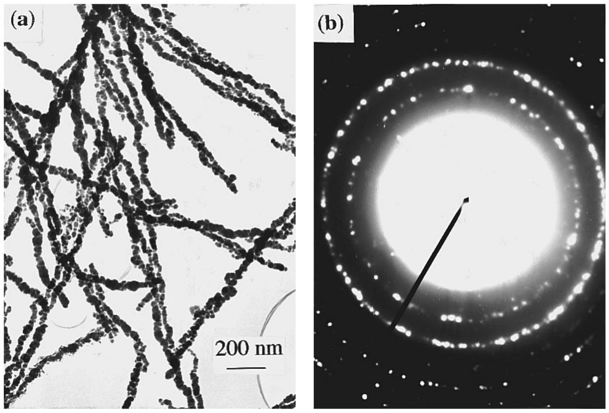

FIG. 2. (a) TEM photograph, and (b) electron-diffraction pattern of randomly oriented chains composed of Fe spheres with particle size of 35 nm.

ICPA data show that the boron content in the samples is small (<8 at. %). Also, the boron content was found to decrease as the particle size increases. For example, the boron content is about 8 at. % at a particle size of 20 nm and <3 at. % at 70 nm. The relatively lower boron contents (<8 at. %) in our samples seem to help to achieve crystalline samples.

Since the Fe particles are crystalline in nature as indicated by x-ray and electron diffractions, one would expect the magnetic moments of the spheres to point along the easy axis of magnetization. However, no preferred crystal direction could be noticed to lie along the chain direction with convergent electron-beam diffraction. This could be due to a fanning configuration of the easy axis of magnetization as shown in Fig. 1. As the spheres grow on the adjacent spheres to give chains, the energy minimum may play a role in aligning the easy axis of magnetization on the adjacent spheres. Jacobs and Bean[1] treated each sphere as a dipole of moment μ and diameter a in the chain of spheres model and showed their energy to be

$$W=(\mu_i\mu_j/r_{ij}^3)[\cos(\theta_i-\theta_j)-3\cos\theta_i\cos\theta_j], \qquad (1)$$

where μ_i and μ_j are the adjacent dipoles separated by a distance of r_{ij} and making angles of θ_i and θ_j with the vector joining them. Equation (1) suggests that a fanning configuration can keep the energy minimum.

We find that the one-dimensional chains are formed only when the borohydride-reduction reaction is carried out in the presence of an applied magnetic field. Also, the chains are formed only with lower borohydride concentrations. Higher borohydride concentrations lead to higher boron contents and amorphous nature and to an increase in self-nucleation. These observations suggest that crystalline anisotropy, magnetostatic interactions, and suppression of self-nucleation may all play a role in the formation of chains.

B. Magnetization and coercivity

The variation of saturation magnetization M_s with the particle size (diameter of Fe spheres) is shown in Fig. 3. M_s

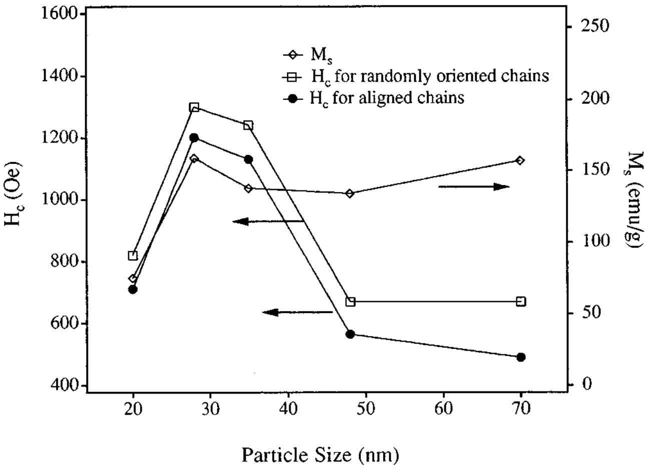

FIG. 3. Variations of saturation magnetization M_s and coercive force H_c with particle size.

increases initially with particle size and remains more or less constant around 150 emu/g for particle size $\geqslant 28$ nm. The lower M_s value below 28 nm is due to the presence of some superparamagnetic Fe spheres at smaller particle size. The observed M_s value of 150 emu/g for particle size $\geqslant 28$ nm is lower than the theoretical value of 218 emu/g for bulk Fe. This difference could be due to the presence of some boron in our samples and surface oxidation of the chains.

Figure 3 also shows the variations of coercive force H_c with particles size for both randomly oriented and aligned chains. H_c increases rapidly initially with particle size, reaches a maximum in the size range 28–35 nm, decreases abruptly in the size range 35–48 nm, and remains constant thereafter in the size range 48–70 nm. This experimentally observed trend in the variation of H_c with particle size is similar to the qualitative plot predicted by Kronmüller.[8] The lower H_c value below 28 nm is due to the presence of some superparamagnetic Fe spheres, which is consistent with the M_s data. The 28–35 nm size range with a nearly constant and maximum value of H_c (1250 Oe) corresponds to the single-domain region in which magnetization reversal takes place by a uniform, homogeneous rotation process. The rapid decrease in H_c in the range 35–48 nm is due to a beginning of a transition from single-domain to multidomain Fe spheres. This transition range is higher than the theoretical critical size of 15 nm predicted in general for particles or grains.[9] However, our results are similar to the experimentally observed size ranges (30 nm) for single-domain region.[6,7] The 48–70 nm size range with a nearly constant but a lower value of H_c (650 Oe) corresponds to the multidomain region in which magnetization reversal takes place by domain-wall motion.

We see that in the single-domain (28–35 nm) region, the H_c values do not vary significantly with particle size. The insensitivity of H_c with particle size supports the fanning configuration of the Fe spheres in the chain in the single-domain region. Both curling and buckling configurations are expected to show changes in H_c, while both fanning and coherent configurations are expected to show no variation in H_c with particle size;[10] but the coherent configuration is expected to have a much larger H_c than fanning configuration (see later). It should be noted that the chain of spheres model is, however, not applicable for the multidomain region as the model neglects the anisotropy field $2K_1/M_s$, where K_1 is the anisotropy constant. For Fe, $2K_1/M_s \approx 540$ Oe and can be neglected in the single-domain region as $2K_1/M_s \ll H_c$ (1200 Oe). But it cannot be neglected in the multidomain region as $2K_1/M_s$ is comparable to the observed H_c values (650 Oe).

Jacobs and Bean[1] showed that the coercive force for a symmetric fanning configuration of single-domain particles can be given as

$$H_{c,n}=(\mu/a^3)(6K_n-4L_n), \tag{2}$$

where $H_{c,n}$ is the coercive force of the chain with n particles, and μ and a are, respectively, the dipole moment and diameter of the spherical particles. The term μ/a^3 is also related to the saturation magnetization I_s per unit volume as

$$\mu/a^3=\pi I_s/6. \tag{3}$$

The values of K_n and L_n are given by the following summation terms as:

$$L_n=\sum_{j=1}^{(1/2)(n-1)<j\leqslant(1/2)(n+1)} [n-(2j-1)]/n(2j-1)^3, \tag{4}$$

$$M_n=\sum_{j=1}^{(1/2)(n-2)<j\leqslant(1/2)n} (n-2j)/n(2j)^3, \tag{5}$$

and

$$K_n=L_n+M_n. \tag{6}$$

Knowing that $\pi I_s/6$ is about 900 Oe for pure Fe, Jacobs and Bean[1] calculated and tabulated H_c for various numbers of spheres n in the chains.

Using these tabulated theoretical values of H_c for the symmetric fanning mechanism and $(\mu/a^3)=900$ Oe in Eq. (2), we obtained the values of $(6K_n-4L_n)$ for various values of n. Using these values of $(6K_n-4L_n)$, the observed M_s values of 159 and 138 emu/g, respectively, for the particle sizes of 28 and 35 nm for aligned chains, and the observed density of 7.0 g/cm^3, we then calculated the H_c values for our samples. Although H_c increases with n, the increase becomes less and less significant as n increases. For example, the difference in H_c between $n=6$ and 12 is about 300 Oe. The calculated H_c values for an average of $n=8$ spheres in the chains are 1400 and 1214 Oe, respectively, for the particle sizes of 28 and 35 nm. Our experimentally observed values of 1200 and 1130 Oe, respectively, for the particle sizes of 28 and 35 nm are close to these expected values of H_c for symmetric fanning mechanism. A small difference between the observed and expected values could be due to imperfections in spheres and interchain interactions among the aligned chains. Thus the observed H_c values support the fanning mechanism and rule out coherent mechanism as the latter is expected to show much higher $H_c \approx 5000$ Oe.

Another important difference among different mechanisms is the comparison between the coercive force H_c of aligned chains (when the angle Ψ between the aligned chains and the applied magnetic field is zero) and the coercive force

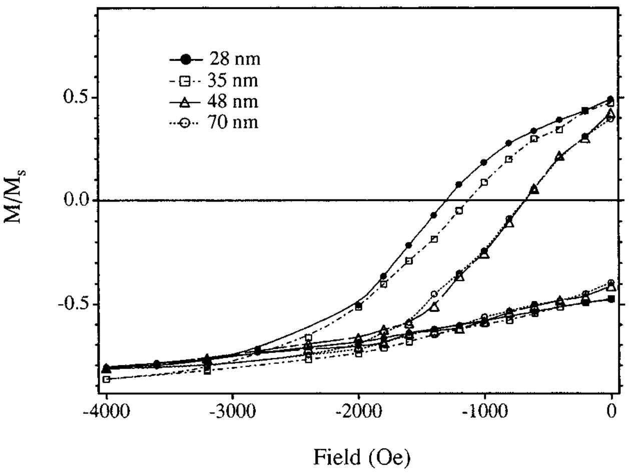

FIG. 4. Hysteresis loops of randomly oriented chains with different particle sizes.

$\overline{H_c}$ of randomly oriented chains.[1] In the case of fanning mechanism, H_c is only slightly higher than H_c while for coherent mechanism, H_c is much lower than H_c. For example, the relationship between H_c and H_c for fanning mechanism is given below for $n=2$ and $n=\infty$: For $n=2$,

$$\overline{H_c}=(1.13\pm0.02)(2K_2\mu/a^3)=1.13H_c(\Psi=0) \qquad (7)$$

and for $n=\infty$,

$$\overline{H_c}=(1.35\pm0.03)(2K_\infty\mu/a^3)=1.08H_c(\Psi=0), \qquad (8)$$

where K_n, μ and a are as defined before. From the experimental results of Fig. 2, we find $H_c/H_c(\Psi=0)=1.083$ at the particle size of 28 nm and $H_c/H_c(\Psi=0)=1.097$ at the particle size of 35 nm, which are in good agreement with the expected values of Eqs. (7) and (8) for the fanning mechanism.

C. Remanence

Figure 4 compares the hysteresis loops of randomly oriented chains for various particle sizes. First, as we discussed before, the hysterisis loop is insensitive to particle size in both the single-domain (28–35 nm) and multidomain (48–70 nm) regions. Second, the remanence is about 0.5 in the single-domain region, which is in agreement with the theoretical value of the fanning mechanism.[1] The remanence is about 0.4 in the multidomain region, which is due to the influence of multidomain characteristics on the magnetization reversal.

Figure 5 compares the hysterisis loops of aligned chains in the single-domain and multidomain regions. The loop for 35 nm was similar to that for 28 nm, while the loop for 48 nm was similar to that for 70 nm. Therefore, the loops for only 28 and 70 nm are shown in Fig. 5. The aligned chains show lower remanence than the theoretical value of 1.0 which could be due to imperfections both in the spheres and alignment, and interchain interactions. Also, a slightly higher remanence is found with larger particle size (70 nm) compared to that with the smaller particle size (28 nm). This could be due to a higher aspect ratio for larger particle size as we find the larger particle size to give longer chains with our synthesis procedure. However, it could also be due to a complex role of particle shape and morphology, as suggested by Smyth *et al.*[11]

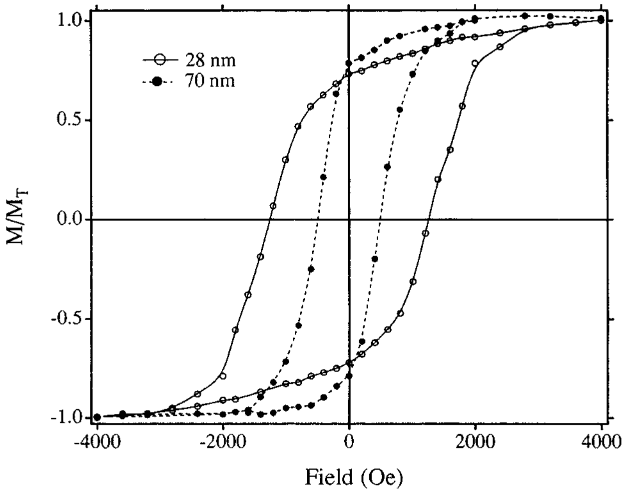

FIG. 5. Hysteresis loops of aligned chains having particle sizes of 28 and 70 nm. The chains were aligned parallel ($\Psi=0$) to the applied field during the measurement.

D. Angular dependence of H_c and loop shape

Figure 6 shows the angular dependence of the switching field H_c for different particle sizes. The angular dependence was studied by mounting the aligned chains at different angles Ψ to the applied magnetic field. Two important features can be noticed from the data of Fig. 6. First, both H_c and its angular dependence do not change with particle size in both the single-domain region (28–35 nm) and in the multidomain region (48–70 nm). Second, H_c increases with increasing Ψ up to about $\Psi\approx70°$ and thereafter decreases with Ψ in both the single-domain and multidomain regions. This trend in angular dependence in the single-domain region is similar to that expected for the fanning mechanism and dif-

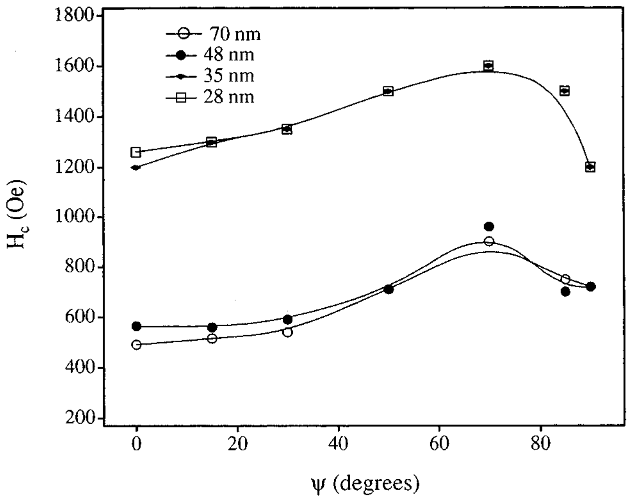

FIG. 6. Angular (Ψ) dependence of H_c for aligned chains having different particle size. Ψ is the angle between the aligned chains and the direction of applied magnetic field.

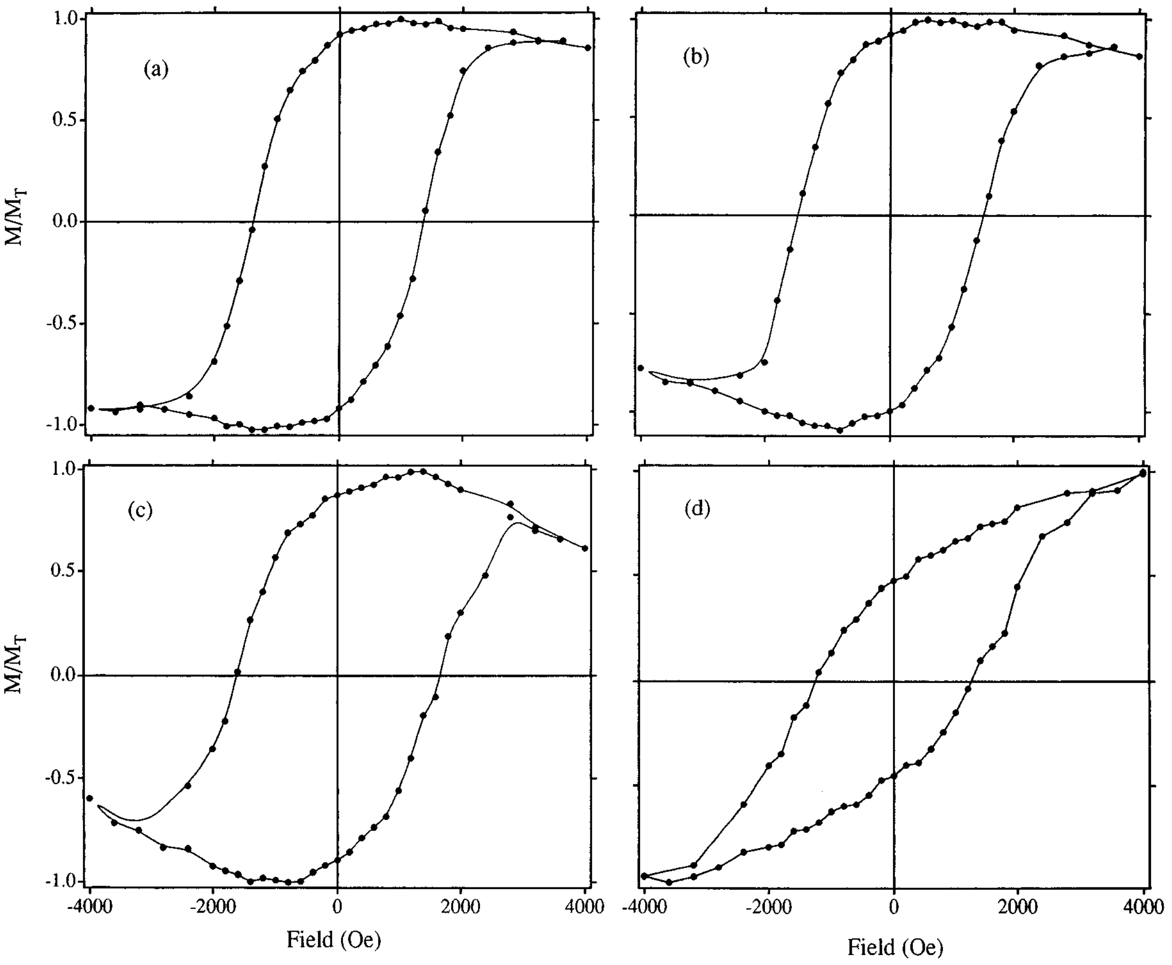

FIG. 7. Hysteresis loops recorded at different angles Ψ for aligned chains with a particle size of 28 nm: (a) 30°, (b) 50°, (c) 70°, and (d) 90°.

ferent from that expected for coherent mechanism.[1] In the former mechanism, H_c is expected to increase gradually with Ψ up to $\Psi \approx 50°$ and then decrease rapidly and reach 0 at $\Psi = 90°$, while in the latter mechanism, H_c is expected to decrease with Ψ. However, the maximum in H_c occurs around 70° in the experimental data and H_c does not reach zero at 90°. This difference could be due to imperfect alignment of the chains and interchain interactions.

In addition, the angular dependence of H_c is significantly different from that found for bar-shaped and acicular particles.[3,11] In the case of acicular and bar-shaped particles, H_c remains almost constant up to about 50° and then increases dramatically. This difference suggests that although the fanning model has been used for a long time to explain the lower H_c values of acicular particles, the reversal mechanism might be significantly different for acicular particles and the true chains of spheres.

The shapes of the hysterisis loops recorded at different Ψ values (30, 50, 70, and 90°) are compared in Fig. 7 for the sample with the particle size of 28 nm. The loop recorded at $\Psi = 0$ is available in Fig. 5 for the same particle size. There is no significant change in the shape of the loop as the angle Ψ changes from 0 to 70°. Although the shape of the loop recorded at $\Psi = 90°$ is significantly different from those recorded at $\Psi < 90°$, H_c does not fall to zero due to interchain interactions and imperfect alignment of chains as discussed earlier. Surprisingly, the observed results of the loop shape do not follow that predicted by Jacobs and Bean[1] for the symmetric fanning model. In the fanning model, the remanence is expected to decrease rapidly with Ψ. The observed trend in the shape variation with Ψ is similar to that found for bar-shaped Permalloy particles.[11] The reason for this is not clear at the moment and it needs further investigation.

IV. CONCLUSIONS

Ferromagnetic chains composed of nanometer size spheres of crystalline Fe have been obtained by an inexpensive chemical method. The chains could be obtained over a range of particle size (20–70 nm) by controlling the synthesis conditions. Saturation magnetization as high as 160 emu/g and coercive force as high as 1300 Oe could be achieved. Magnetic properties have been investigated in the single-domain (28–35 nm) and multidomain (48–70 nm) regions. The variation of H_c with particle size is in agreement with the qualitative predictions of Kronmüller.[8] The observed magnetic properties in the single-domain region have been compared with the predictions of the chain of spheres model of Jacobs and Bean.[1] The observed values of H_c and their variations with particle size support a fanning model for magnetization reversal. The fanning mechanism is also supported by the relationship between the coercivities of randomly oriented and aligned chains, and the angular dependence of H_c. This study represents an experimental fabrication of the true chain of spheres of ferromagnetic metal particles and a comparison of their magnetic properties with the theoretical models available in the literature.

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[*] To whom correspondence should be addressed.

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