Magnetic hysteresis anomalies in ferritin

Salah A. Makhlouf* and F. T. Parker
Center for Magnetic Recording Research, University of California, San Diego, La Jolla, California 92093-0401

A. E. Berkowitz
Center for Magnetic Recording Research, University of California at San Diego, La Jolla, California 92093-0401
and Department of Physics, University of California, San Diego, La Jolla, California 92093
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Ferritin, an antiferromagnetic nanoparticle with a net magnetic moment, exhibits some unusual magnetic behavior. Above its blocking temperature, $T_B \approx 12$ K, the magnetization can be fit with the Langevin function only by including an additional linear term. The saturation moment decreases linearly with increasing temperature, and suggests an ordering temperature of about 460 K. Below T_B, both zero-field-cooled and field-cooled hysteresis loops exhibit large coercivity (~ 1800 Oe) and irreversibility in the loops is found up to $H = 35$ kOe. An exchange field H_e of few hundred Oe is observed at low temperatures. The dependencies of H_e and H_c on temperature were also studied. [S0163-1829(97)52022-4]

INTRODUCTION

Ferritin is the iron-storage protein of mammals, plants, and several bacteria; it functions to maintain iron in an available nontoxic form.[1] The molecule consists of an iron oxyhydroxide core ≈ 70 Å diam, surrounded by an ≈ 120 Å diam external protein shell. The structure of the hydrous ferric oxide in mammalian ferritin is a hydrous ferric oxide phosphate with nominal formula $(FeOOH)_8(FeOH_2PO_4)$ and resembles that of the mineral ferrihydrite.[2] The antiferromagnetic ordering temperature of natural horse spleen ferritin was reported to be ≈ 240 K.[2,3] Mössbauer spectra of ferritin at low temperatures display broad sextets.[4]

With its large surface/volume ratio, a magnetic moment arising from uncompensated spins, and its roughly monodispersed nature, ferritin provides an excellent noninteracting antiferromagnetic (AF) nanoparticle system.[5–9] In the present study, we report on the magnetic properties of horse spleen ferritin, with emphasis on hysteresis, exchange anisotropy, and ordering temperature.

EXPERIMENTAL PROCEDURES

The sample was horse spleen ferritin, Ferritin type I, obtained from the Sigma Chemical Company. Samples were dried on a glass slide in air for ~ 24 h, removed from the slide, and immobilized in epoxy for magnetization measurements in a commercial superconducting quantum interference device (SQUID) magnetometer.

RESULTS AND DISCUSSION

Figure 1 shows 50 Oe field-cooled (FC) and zero-field-cooled (ZFC) magnetizations as functions of temperature. The ZFC curve exhibits a maximum at about 12 K, and the ZFC and FC curves bifurcate at ~ 20 K. In a particle system such as this one, deviations from a monodispersed condition exist. The resulting distribution of anisotropy energies gives rise to a distribution in blocking temperature, T_B. The maximum in the ZFC curve at 12 K may be considered the average T_B. Various investigators have reported values of 11–13 K for the average blocking temperature of horse spleen ferritin obtained by magnetization measurements.[6,10] The maximum blocking temperature of ~ 20 K (bifurcation point) relates to the largest particles in the sample.

Magnetization curves were measured at temperatures above T_B in fields up to 55 kOe. Typical magnetic isotherms are shown in Fig. 2. Magnetization curves vs H/T at temperatures above the bifurcation temperature do not superimpose. This behavior is quite different from that usually observed for very small ferro- and ferrimagnetic particles;[11] however, it is similar to that reported for AF NiO nanoparticles.[12] Since the data do not fit the simple Langevin function expected for superparamagnetic samples above

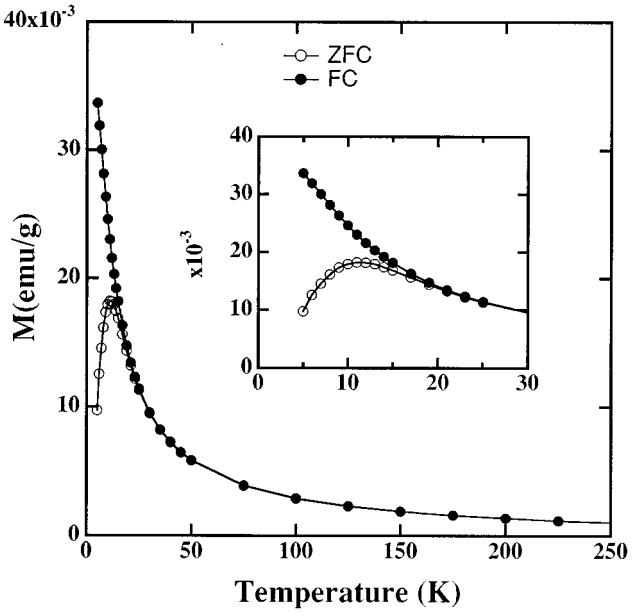

FIG. 1. Magnetization for ZFC and FC ferritin in 50 Oe applied field as a function of temperature.

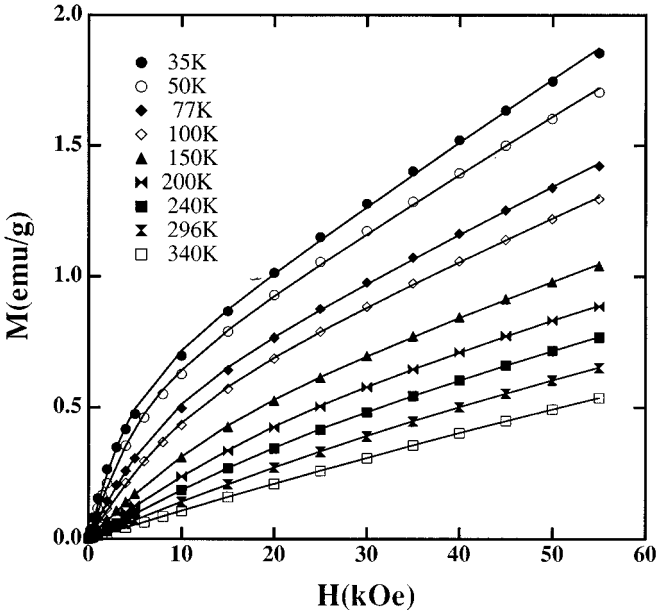

FIG. 2. Magnetization as a function of applied field at the indicated temperatures. Solid lines are the fits.

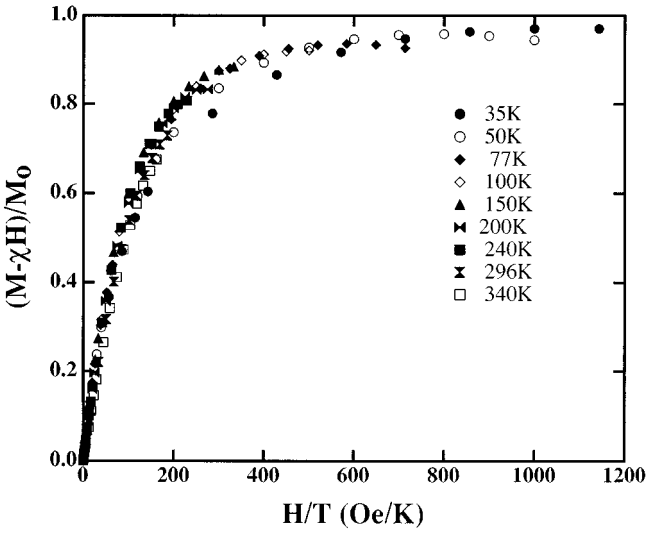

FIG. 4. $(M-\chi H)/M_0$ vs H/T for ferritin.

T_B, we have fit the magnetization curves by a modified formula:[7] $M=M_0[\coth(x)-1/x]+\chi H$. Here, M_0 is the saturation magnetization (in emu/g); $x=\mu_p H/\mathrm{kT}$, where μ_p is the average magnetic moment of the ferritin core arising from uncompensated spins; and χ is the susceptibility. χ decreases with increasing temperature as shown in Fig. 3. As noted by Néel,[13] χ in AF nanoparticles can have two sources. One is the bulk susceptibility of randomly oriented AF grains. The other develops below the blocking temperature. It arises from the couple exerted by the applied field on AF nanoparticles with even numbers of ferromagnetic spin planes. The result is a progressive rotation of the AF axis from one end of the particle to another. The additional susceptibility is estimated by Néel to be of the order of the bulk value and strongly temperature dependent, features which are consistent with Fig. 3. Subtracting the linear portions and normalizing by M_0, $[(M-\chi H)/M_0]$ vs H/T data fit on a universal curve, as shown in Fig. 4. This implies that interparticle interactions are negligible and that μ_p is $\approx$ constant. Figure 5 shows the temperature dependence of M_0 and μ_p obtained from the fits. μ_p is $\approx$ constant, and M_0 decreases linearly with increasing temperature. One possible explanation for this unusual dependence is that M_0 originates from surface moments. Surface moments should vary linearly with T_N-T near T_N, where T_N is the Néel temperature.[14] We found, using molecular-field calculations, that the linearity holds well down to $T/T_N=0.2$.[15] Linear extrapolation to $M_0=0$ suggests an ordering temperature of about 460 K

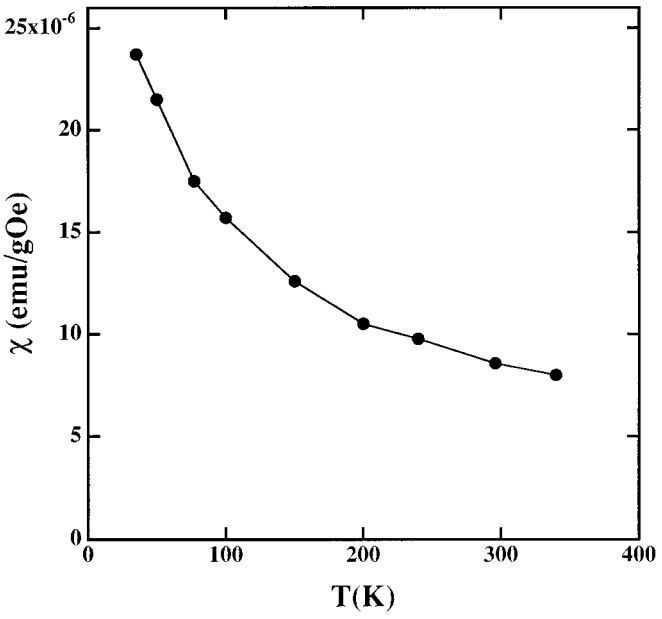

FIG. 3. Temperature dependence of χ for ferritin.

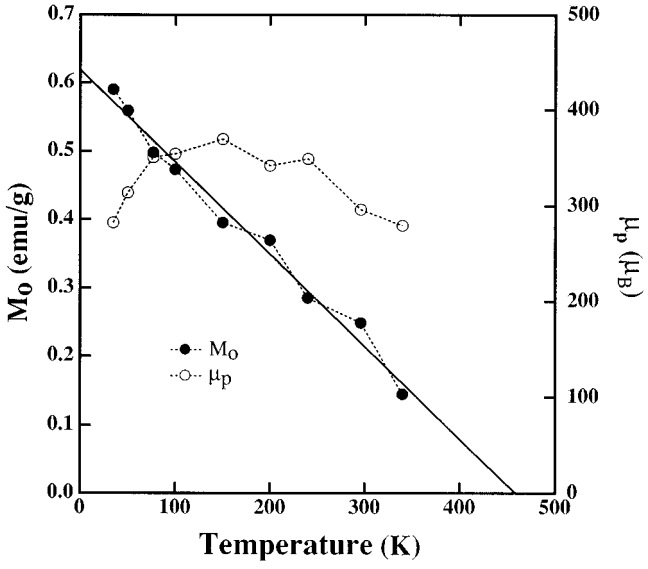

FIG. 5. Temperature dependencies of M_0 and μ_p for ferritin. Dashed lines are guides to the eye. Solid line is the fit.

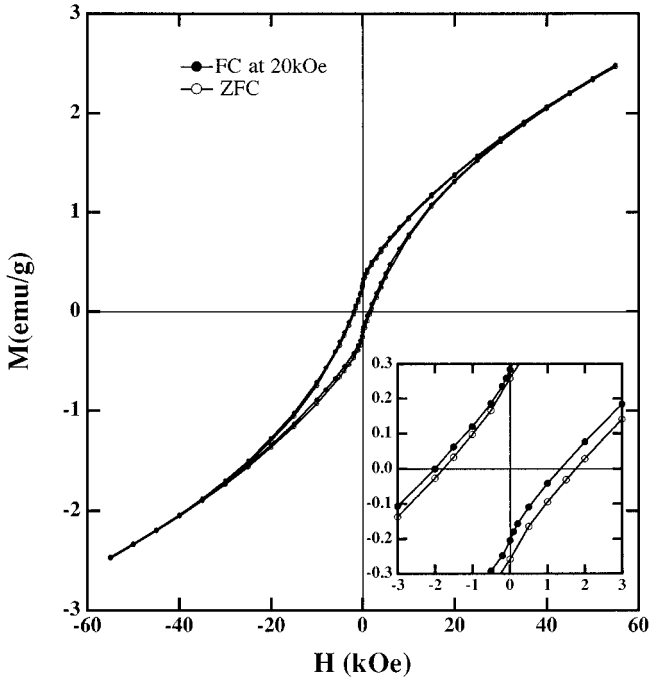

FIG. 6. Hysteresis loops at 5 K of ZFC and FC ferritin in 20 kOe. Inset is an expansion of the central portion of the loops.

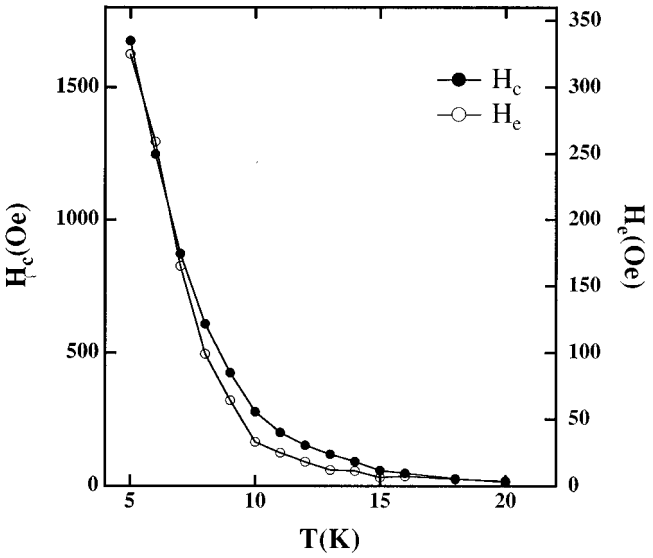

FIG. 7. Exchange field H_e and coercive force H_c as functions of temperature for ferritin after FC in 20 kOe.

which is much higher than the reported value of $T_N = 240$ K for ferritin obtained by using indirect methods.[2,3] We have also observed a similar linear temperature dependence of M_0 for 53 Å diameter AF NiO particles.[12,15] The very slow decrease of μ_p compared with that of the saturation moment M_0 might be due to the formation of new uncompensated moments via thermal disorder.[7]

Figure 6 shows FC and ZFC hysteresis loops measured at 5 K. A large coercivity, $\sim$1800 Oe at 5 K, is present; the magnetization is increasing at $H = 55$ kOe; and the loop is open up to $> \sim 30$ kOe, as observed by other investigators.[7,16] Extrapolation back to $H = 0$ of the ZFC magnetization vs field curve for $H \geq 30$ kOe gives an intrinsic magnetization of 0.836 emu/g. When saturated with iron, the radius of the core is 40 Å and it has a molecular weight of 680000 amu,[17] giving $\sim 2.6 \times 10^{17}$ particles/gm. This implies a magnetic moment per particle, $\mu_p = 345 \mu_B$, in agreement with the high-temperature values obtained from the superparamagnetic behavior (see Fig. 5). Néel[18] has predicted that antiferromagnetic materials will have a net moment from uncompensated spins. Hence the magnetic moment per particle can be written as $\mu_p = N_{\rm uc} \mu_i$, where μ_i is the magnetic moment per iron ion and $N_{\rm uc}$ is the number of uncompensated spins per particle. Using $5 \mu_B$ per Fe^{3+} ion, one gets $N_{\rm uc} = 70$ ions. Since the ferritin core can store up to a maximum of $N_{\rm Fe} \approx 4500$ iron ions, $N_{\rm uc} \sim 5\%$ of the surface ions. $N_{\rm uc}$ is also approximately the square root of the total number of ions, consistent with previous results obtained for ferritin[7] and amorphous ferric gel particles.[19] The fact that $N_{\rm uc} \approx (N_{\rm Fe})^{1/2}$ suggests a random arrangement of uncompensated sites in the AF nanoparticles. The broad Mössbauer spectra could arise from this random site occupancy. Thus these data do not permit a clear assignment of uncompensated spin locations (or vacant spin lattice sites), i.e., they are consistent with either surface or core sites.

A hysteresis loop measured after FC in 20 kOe is shown in Fig. 6. The loop is irreversible for fields up to $\sim$35 kOe. A loop displacement, or exchange field H_e (in exchange anisotropy[20] terminology), of $\sim$325 Oe at 5 K is present. The temperature dependencies of H_c and H_e for the FC case are shown in Fig. 7. Both H_c and H_e decrease rapidly with increasing temperature from 5 to 12 K, and more slowly for $12 \leqslant T \leqslant 20$ K, and both are negligibly small for $T > 20$ K, the bifurcation temperature in Fig. 1. This loop shift is similar to that of spin glasses after FC below the freezing temperatures.[21] The spin frustration associated with this behavior could arise from vacant spin-lattice sites, as discussed above.

SUMMARY

Horse spleen ferritin exhibits anomalous magnetic properties associated with uncompensated spins either on the surface or in the core of these AF nanoparticles. The magnetic moment per ferritin molecule is $\mu_p \approx 345 \mu_B$, representing $\sim 5\%$ of the moments of the surface ions. Saturation moment decreases linearly with increasing temperature and extrapolates to an ordering temperature of $\sim$460 K. Samples FC below the blocking (or freezing) temperature exhibit high coercivity and shifted loops.

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*Permanent address: Department of Physics, Faculty of Science, Assiut University, Assiut 71516, Egypt.

[1] S. J. Lippard *et al.*, J. Am. Chem. Soc. **109**, 3337 (1987).

[2] S. H. Bell *et al.*, Biochim. Biophys. Acta **787**, 227 (1984).

[3] E. P. Bauminger and I. Nowik, Hyperfine Interact. **50**, 489 (1989).

[4] K. M. Towe and W. F. Bradley, J. Colloid Interface Sci. **22**, 384 (1967).

[5] M.-E. Y. Mohie-Eldin, R. B. Frankel, and L. Gunther, J. Magn. Magn. Mater. **135**, 65 (1994).

[6] S. Gider, D. D. Awschalom, T. Douglas, S. Mann, and M. Chaparala, Science **268**, 77 (1995).

[7] S. H. Kilcoyne and R. Cywinski, J. Magn. Magn. Mater. **140**, 1466 (1995).

[8] D. P. E. Dickson, N. M. K. Reid, and C. Hunt, J. Magn. Magn. Mater. **125**, 345 (1993).

[9] C. Hunt, Q. A. Pankhurst, and D. P. E. Dickson, Hyperfine Interact. **91**, 821 (1994).

[10] J. Tejada and X. X. Zhang, J. Phys., Condens. Matter **6**, 263 (1994).

[11] I. S. Jacobs and C. P. Bean, in *Magnetism*, Vol. III, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), p. 294.

[12] Salah A. Makhlouf, F. T. Parker, F. E. Spada, and A. E. Berkowitz, J. Appl. Phys. (to be published).

[13] L. Néel, C. R. Acad. Sci. **252**, 4075 (1961); **253**, 9 (1961); **253**, 203 (1961); **253**, 1286 (1961).

[14] D. L. Mills, Phys. Rev. B **3**, 3887 (1971).

[15] Salah A. Makhlouf, F. T. Parker, and A. E. Berkowitz (unpublished).

[16] S. Gider, D. D. Awschalom, T. Douglas, K. Wong, and S. Mann, J. Appl. Phys. **79**, 5324 (1996).

[17] C. C. Ford *et al.*, Philos. Trans. R. Soc. London, Ser. B **304**, 551 (1984).

[18] L. Néel, in *Low Temperature Physics*, edited by C. Dewitt, B. Dreyfus, and P. D. de Gennes (Gordon and Breach, New York, 1962), p. 413.

[19] J. M. D. Coey and P. W. Readman, Nature (London) **246**, 476 (1973).

[20] W. H. Meiklejohn and C. P. Bean, Phys. Rev. **102**, 1413 (1956); **105**, 904 (1957); W. H. Meiklejohn, J. Appl. Phys. **33**, 1328 (1962).

[21] E.g., P. Monod, J. J. Préjean, and B. Tissier, J. Appl. Phys. **50**, 7324 (1979).