Size dependence of the spin-flop transition in hematite nanoparticles

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The spin-flop transition of acicular hematite nanoparticles of different size synthesized by chemical route and annealed at different temperatures has been investigated as a function of temperature. Transmission electron microscopy (TEM) measurements show that particles have an ellipsoidal shape, with a major axis of 330 ± 50 nm and a minor axis of 70 ± 10 nm. TEM and x-ray diffraction experiments show that nanoparticles are made of hematite crystallites, which grow on increasing the annealing temperature. Both the Morin transition temperature (T_M) and the spin-flop transition field (H_{sf}) have been found to increase for increasing crystallite size (d): for instance, for d=36 nm particles $T_M=164$ K and the value of H_{sf} extrapolated at T=0 (H_{sf0}) is 1.7 T, whereas for bulk hematite $T_M=263$ K and $H_{sf0}=6.5$ T. Both H_{sf0} and T_M follow a 1/d dependence (at a faster rate for H_{sf0}), indicating that their variation is mainly driven by surface effects.

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Nanoscale confinement gives rise to magnetic behaviors that may differ strongly in several aspects from those observed on conventional bulk materials. In nanoparticles, the magnetic properties are mainly governed by finite-size and surface effects, the latter becoming more and more important as the particle size decreases, due to the increase of the surface to volume ratio.¹ Indeed, the structural and electronic properties are modified near and at the surface, resulting in a breaking of lattice symmetry and broken bonds, giving rise to site-specific surface anisotropy, weakened exchange coupling, and surface spin disorder.² Moreover, spin coupling at the interface between different surface and core magnetic structures can give rise to exchange anisotropy.³

Finite-size and surface effects are peculiar in antiferromagnetic nanoparticles. As shown by Néel in his seminal works,⁴ as the particle size decreases, a net magnetic moment is produced due to the nonexact compensation of the two magnetic sublattices, i.e., imbalance in the number of "up and down" spins. For nanoparticles, a superparamagnetic susceptibility, due to uncompensated spins, can dominate over the antiferromagnetic contribution itself. Because of the structural disorder and broken bonds, the surface spin directions deviate at the surface from the antiferromagnetic alignment, strongly affecting the magnetic anisotropy. Experimental work by Makhlouf et al.⁵ showed that NiO nanoparticles could exhibit remarkable hysteresis at low temperature, having coercivities and loop shifts up to 10 kOe. Atomic modeling^{6,7} indicated that, as a result of a finite-size effect, the reduced coordination of surface spins allows a variety of reversal upon cycling the applied field, resulting in the observed large coercivities, loop shifts, and high field irreversibility.

It is well known that when a magnetic field is applied to an antiferromagnet, a significant change in the spin configuration may occur. For a simple uniaxial antiferromagnet, when a large enough magnetic field is applied along the preferred axis, the so-called *spin-flop* reorientation transition occurs, i.e., a 90° rotation of the sublattice vectors. The spinflop transition field (H_{sf}) of an antiferromagnet has the form^{8,9}

$$H_{sf}^2 = \frac{2K}{(\chi_\perp - \chi_\parallel)},\tag{1}$$

where *K* is the anisotropy constant and χ_{\perp} and χ_{\parallel} are the perpendicular and parallel susceptibilities, respectively. As in a pure uniaxial antiferromagnet χ_{\perp} is temperature independent below the Néel temperature, and the $H_{sf}(T)$ behavior is essentially related to the temperature dependence of χ_{\parallel} and *K*. At *T*=0, the critical magnetic field at which the rotation occurs, H_{sf} , is given by

$$H_{sf0} = (2H_E H_A - H_A^2)^{1/2}, (2)$$

where H_E is the exchange field and H_A is the anisotropy field. In magnetic particles, both the intraparticle exchange interactions and magnetic anisotropy are size dependent; hence a significant size dependence is expected for H_{sf} .

In such context, α -Fe₂O₃ (hematite) deserves a particular attention, although it is not an archetypal antiferromagnetic system. Indeed, below the Néel transition (T_N =960 K), the bulk material shows a first-order magnetic transition at T_M = 263 K, the Morin transition. Basically, below T_M , the material behaves as a uniaxial antiferromagnet (AF), with spins oriented along the trigonal [111] axis (*c* axis), whilst above it the spins lie in the basal plane (perpendicular to [111] axis) except for a slight spin canting (~1 min of arc) out of the plane,^{10,11} which gives rise to the small net weakferromagnetic (WF) moment. The small canting of moments

TABLE I. Crystalline size, Morin temperature (T_M) and spinflop transition field at T=0 values for the hematite nanoparticles after thermal treatments.

Sample	Annealing temperature (°C)	Crystalline size (nm)	Т _М (К)	H_{sf0} (T)
FAC650	650	36.4	186(3)	1.7(2)
FAC750	750	40.0	200(5)	2.5(2)
FAC850	850	82.7	243(3)	5.4(2)
FAC1000	1000	159	261(3)	6.6(2)

results from the anisotropic exchange interaction, the Dzialoshinski-Moriya interaction.^{12,13} The Morin transition arises from a competition between the local ionic anisotropy term from spin-orbit coupling and the long-range dipolar anisotropy term.¹⁴ Such anisotropy terms have a comparable magnitude, opposite signs, and different temperature dependencies. At the Morin transition temperature, a change of the sign of the total free energy occurs and causes the spinflip of the AF lattice.

The Morin temperature was found to be strongly dependent on particle size, decreasing with it and tending to vanish below a diameter of ~ 8 nm, for spherical particles.¹⁵ Strains, crystal defects (e.g., low crystallinity of the particles, vacancies), stoichiometry deviations, and surface effects have been indicated as a cause of the reduction of T_M .¹⁶ In principle, as these features affect both H_E and H_A fields, a reduction of the spin-flop field with respect to the bulk value [6.75 T (Ref. 17)] is also expected. To our knowledge, no detailed investigation and comparison of the size effect on both the Morin temperature and the spin-flop transition field has been reported in the literature so far. In this paper, we have investigated the effect of thermal annealing, strongly affecting the particle size and its degree of crystallinity, on the spin-flop field in acicular hematite particles and we have correlated it to the variation of the Morin temperature.

Hematite acicular particles were obtained by reaction of $2 \times 10^{-2}M$ FeCl₃ and $3.8 \times 10^{-4}M$ NaH₂PO₄ at 60 °C, followed by aging in boiling water for three days. The precipitate was ultracentrifigated and washed several times with water and dried at 50 °C. Thermal treatments were performed by heating the sample at a rate of 1 °C/min to the annealing temperature (Table I) and, after 24 h, cooling the sample at a rate of 1 °C/min down to room temperature.^{18,19}

By means of transmission electron microscopy (TEM) measurements it has been found that particles have an ellipsoidal shape, with a major axis of 330 ± 50 nm and a minor axis of 70 ± 10 nm.¹⁸ Moreover, TEM diffraction experiments show the single-crystal hematite diffraction pattern¹⁸ for the particles both before and after thermal treatment. In particular, TEM and x-ray diffraction show that as-prepared nanoparticles contain a number of crystallites, which grow on increasing the annealing temperature:¹⁸ Table I shows for all the annealing temperatures the crystallite sizes derived by means of Fourier analysis of the full width at half maximum of the most intense x-ray reflections.¹⁸ As the hematite nanoparticles were synthesized from an aqueous medium, the presence of water, OH radicals, and phosphate anions be-



FIG. 1. Magnetization as a function of temperature for samples annealed at different temperatures (T_A) .

tween crystallites within the particles is expected.^{20,21} Actually, high-resolution electron micrographs of the as-prepared particles show that crystallites are separated by a thin interlayer probably consisting of the residuals of the synthesis process. Moreover, thermal treatments at moderate temperatures lead to the loss of molecular water and to the loss of OH and phosphate groups at higher annealing temperature. Finally, at 1000 °C the crystallites consolidate forming sub-micron units.^{18,19}

Magnetization versus temperature and field measurements were carried out by a commercial SQUID magnetometer in the temperature range 5-300 K, for fields up to 10 T.

Previous investigations¹⁸ on similar samples have shown that the Morin transition, characterized by a rapid increase in the magnetization versus temperature, does not occur in the as-prepared sample whereas it appears after thermal annealing at temperatures above 600 °C, T_M increasing with the annealing temperature T_{ann} (Fig. 1, Table I). This reflects the increase of the crystallite size with increasing T_{ann} . The small maximum observed at $T \sim 75$ K in the magnetization



FIG. 2. Magnetization as a function of magnetic field at temperatures above T_M for samples annealed at $T_A = 750$ °C (FAC750; open symbol; 200 K), and $T_A = 1000$ °C (FAC1000; solid symbols; 290 K). Inset: M(H) curve for the FAC 1000 sample, showing the two linear field behaviors (see text).



FIG. 3. M(H) curves measured at temperatures below T_M : T = 80 K for FAC650; T = 100 K for FAC1000.

versus temperature curve of the sample annealed at 850 °C could be in principle due to the existence of a fraction of much smaller iron oxide particles with blocking temperatures between 60 and 70 K. Magnetization measurements reflect the increase of the crystallite size with increasing T_{ann} . Magnetization measurements as a function of the applied field were performed after zero-field cooling from room temperature, on samples annealed at 650 °C (FAC650 sample), 750 °C (FAC750 sample), 850 °C (FAC850 sample), and 1000 °C (FAC1000 sample). Examples of magnetization curves above T_M are reported in Fig. 2. The magnetization first shows a linear increase with the field, then a downward curvature, and finally an almost linear behavior up to the largest applied magnetic field. This suggests the existence of two contributions to the magnetization $M = M_{nc}(H) + \chi H$. The first term, M_{nc} , is responsible for the rapid increase of the magnetization at low field and tends to saturate; on the other hand, the second term, χH , is responsible for the nonsaturating behavior at high field. This is consistent with the presence of hematite particles whose magnetization is due to the antiferromagnetic structure of the particle core, responsible for the nonsaturating second term, superimposed to a



FIG. 4. M(H) curve measured at T=80 K for sample FAC750. Inset: field derivative of the magnetization at T=80 K; the thick solid line is a smoothing to the data.



FIG. 5. Spin-flop transition magnetic field (H_{sf}) as a function of temperature for FAC650 (solid triangles), FAC750 (solid squares), FAC850 (open circles), and FAC1000 (solid circles). The solid lines are a guide to the eyes.

net magnetic moment due to the intrinsic weak ferromagnetism and to the finite size-induced uncompensated moment.

Magnetization versus field measurements below T_M (80 and 100 K) are reported in Figs. 3 and 4. A change of curvature, signaling the spin-flop transition, is observed to occur in a quite large field range, because of the distribution of particle size and the distribution of antiferromagnetic directions in crystallites. The spin-flop H_{sf} is taken as the field at which a maximum appears in the numerical derivative (dM/dH) of M vs H curves (inset of Fig. 4).

The values obtained at different temperatures are plotted in Fig. 5 for each sample, whereas the extrapolated values at T=0, H_{sf0} , are reported in Table I, showing that $H_{sf}(T)$ increases with the annealing temperature, i.e., with the particle size. The temperature behavior of the spin-flop transition field (Fig. 5) is consistent with that expected from Eq. (1) function. As the anisotropy constant saturates a low tem-



FIG. 6. Spin-flop transition field and Morin transition temperature normalized to their respective bulk values $[h=H_{sf}(T=0)/H_{sf}^{bulk}(T=0)$, open symbol; $t=T_M/T_M^{bulk}$, solid symbol] as a function of the reciprocal of the crystallite size. The solid lines are linear fittings to the data.

perature [i.e., $K/K_{T=0} = (M/M_{T=0})^n$, where *n* is an integer whose value depends on the symmetry of anisotropy energy^{8,22}], the observed low-temperature $H_{sf}(T)$ behavior should be essentially related to the temperature dependence of χ_{\parallel} , which vanishes on decreasing temperature, whereas χ_{\perp} is temperature independent: this is responsible for the weak decrease $H_{sf}(T)$ at very low temperature.

Figure 6 shows plots of both $H_{sf}(T=0)$ and the Morin transition temperature (normalized to their bulk values) as a function of the reciprocal of the crystallite size: the linear behavior observed for both data sets indicates that the change in the transitions should be mainly driven by a surface effect. As a matter of fact, both H_A and H_E are strongly affected by microstructural variations induced at the surface by size reduction. On the other hand, the different slopes indicate that the spin-flop transition field decreases on decreasing size at a faster rate than the Morin temperature, pointing to a stronger sensitivity of H_{sf} to surface effects. Actually this should

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- ¹J.L. Dormann, D. Fiorani, and E. Tronc, Adv. Chem. Phys. **98**, 283 (1997).
- ²R.H. Kodama, J. Magn. Magn. Mater. 200, 359 (1999).
- ³A.E. Berkowitz and Kentaro Takano, J. Magn. Magn. Mater. **200**, 552 (1999).
- ⁴L. Néel, C. R. Hebd. Seances Acad. Sci. **252**, 4075 (1961); **253**, 9 (1961); **253**, 1286 (1961).
- ⁵Salah A. Makhlouf, F.T. Parker, F.E. Spada, and A.E. Berkowitz, J. Appl. Phys. **81**, 5561 (1997).
- ⁶R.H. Kodama, S.A. Makholouf, and A.E. Berkowitz, Phys. Rev. Lett. **79**, 1393 (1997).
- ⁷R. Kodama and A.E. Berkowitz, Phys. Rev. B **59**, 6321 (1999).
- ⁸J. Kanamori, in *Magnetism*, edited by G.T. Rado and H. Suhl (Academic, New York, 1965), Vol. I.
- ⁹K. Yosida, Prog. Theor. Phys. 6, 691 (1951).
- ¹⁰C.G. Shull, W.A. Strauser, and E.O. Wollan, Phys. Rev. 83, 333 (1951).
- ¹¹C. Guilland, J. Phys. Radium **12**, 489 (1951).
- ¹²I.E. Dzyaloshinsky, Sov. Phys. JETP 5, 1259 (1957).

be expected as the surface spins can undergo a spin-flop instability at a field much lower than the bulk value [i.e., $H_{sf}(T=0) = (H_E H_A)^{1/2}$].²³

Summarizing, we have investigated the size and temperature dependence of the spin-flop transition in acicular hematite nanoparticles synthesized by chemical route, and we have compared it to the size dependence of the Morin transition temperature. Results indicate that both $H_{sf}(T=0)$ and T_M decrease with decreasing particle size according to a 1/ddependence, but at a faster rate for $H_{sf}(T=0)$. Such larger size sensitivity of the spin-flop field should be mainly related to surface microstructural characteristics, in particular, the distribution of coordination number for surface spins that determines a variety of reversal paths. This, in turn, affects both the exchange and anisotropy fields.

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¹³T. Moriya, Phys. Rev. **120**, 91 (1960).

- ¹⁴J.O. Artman, J.C. Murphy, and S. Foner, Phys. Rev. **138**, A912 (1965).
- ¹⁵N. Amin and S. Arajs, Phys. Rev. B **35**, 4810 (1987).
- ¹⁶M.Z. Dang, D.G. Rancourt, J.E. Dutrizac, G. Lamarche, and R. Provencher, Hyperfine Interact. **117**, 271 (1998).
- ¹⁷A.H. Morrish, *Canted Antiferromagnetism: Hematite* (World Scientific, Singapore, 1994).
- ¹⁸L. Suber, D. Fiorani, P. Imperatori, S. Foglia, A. Montone, and R. Zysler, Nanostruct. Mater. **11**, 797 (1999).
- ¹⁹L. Suber, A Garcia Santiago, D. Fiorani, P. Imperatori, A.M. Testa, M. Angiolini, A. Montone, and J.L. Dormann, Appl. Organomet. Chem. **12**, 347 (1998).
- ²⁰E. Wolska and U. Schuwertmann, Z. Kristallogr. **189**, 223 (1989), and references therein.
- ²¹M. Ocaña, M.P. Morales, and C.J. Serna, J. Colloid Interface Sci. 171, 85 (1995).
- ²²E. Callen and H.B. Callen, J. Appl. Phys. **36**, 1140 (1965).
- ²³D.L. Mills, Phys. Rev. Lett. **20**, 18 (1968).