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Structural and Magnetic Properties of α-Fe_2O_3 Nanoparticles

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The magnetic properties of α-Fe_2O_3 nanoparticles of different shapes (spherical, rhombohedral and acicular), prepared as powders by a chemical route, have been investigated. The particle size effect on the Morin transition (T_M = 263 K in the bulk system) have been studied by analyzing the temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization. For spherical (average diameter between 10 and 50 nm) and rhombohedral (edge between 30 and 350 nm) particles, the Morin temperature was found to decrease with decreasing particle size and increasing magnetic field. On the other hand, acicular particles (major axis between 300 and 700 nm, minor axis between 70 and 100 nm) do not show the Morin transition, unless annealed.

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INTRODUCTION

Materials present different electrical, magnetic, electro-optical and chemical properties when reduced to sizes in the nanometer range. This is due to the so-called 'size effect', i.e. the change in physical properties when the size becomes comparable with some characteristic microscopic physical lengths, giving rise to quantum phenomena for very small dimensions.[1]

The magnetic properties of antiferromagnetic nanoparticles have been receiving renewed attention in the last few years because of their potential for exhibiting magnetization reversal by quantum tunneling.[2] Moreover, some questions remain open some about their magnetic behavior, the Néel theory never having been carefully verified. The net moment of an antiferromagnetic particle, resulting from the non-exact compensation of the two magnetic sublattices, is very sensitive to the particle size and lattice strain and defects. In antiferromagnetic crystalline (rhombohedral) α-Fe_2O_3, (Néel temperature T_N = 960 K)[3,4] a magnetic phase transition occurs at T_M = 263 K, known as the Morin temperature,[5] characterized by a reorientation of the magnetization of the two spin sublattices from parallel to perpendicular to the [111] axis. Due to the anisotropic superexchange interaction,[6,7] spins are slightly (approx. 1°) canted out of the basal plane, giving rise to a weak ferromagnetic state.[8]

In nanoparticles, particle size, lattice strain and defects have a strong influence on the Morin temperature T_M. So far, this effect has been investigated mainly in spherical particles.[9–11] In this context, we have investigated the effect of size on the Morin transition of α-Fe_2O_3 particles, by

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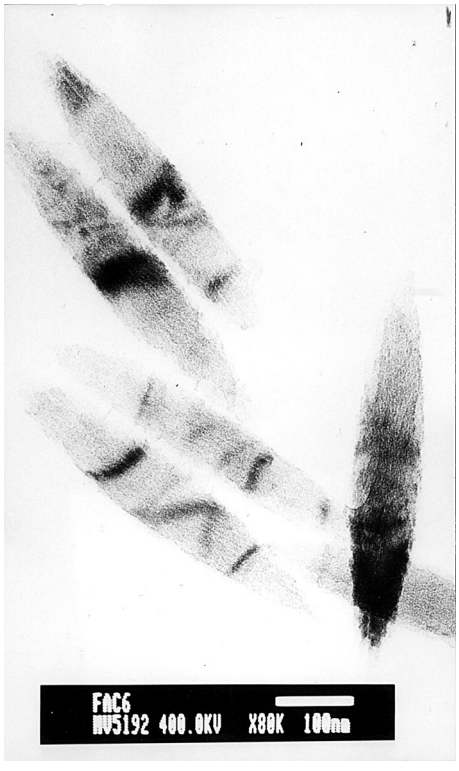

Figure 1 TEM micrograph of acicular α-Fe_2O_3 nanoparticles as prepared.

studying the magnetic properties of fine powders consisting of rhombohedral and acicular particles.

EXPERIMENTAL

Rhombohedral and acicular particles were prepared by reaction of $FeCl_3$ with HCl and NaH_2PO_4, respectively, in H_2O at 100 °C as reported in literature.[12–15] By reaction of mixtures ranging from 5×10^{-3} M $FeCl_3$ and 10^{-3} M HCl to 3×10^{-2} M $FeCl_3$ and 5×10^{-3} M HCl for 24 h in water at 100 °C, rhombohedral particles with edges varying between 30 and 350 nm were obtained. Acicular particles with a major axis of *ca.* 90 nm and a minor axis of *ca.* 25 nm, and a major axis of 500 nm ca. and a minor axis of *ca.* 90 nm were separated after reaction of 10^{-2} M $FeCl_3$ and 2.6×10^{-4} M NaH_2PO_4, and 2×10^{-2} M $FeCl_3$ and 3.8×10^{-4} M NaH_2PO_4, respectively, in boiling water for three days. The precipitate was ultracentrifuged and washed several times with water. The powder was then dried overnight at 50 °C. The thermal treatment was performed by heating the sample at a rate of 3 °C min^{-1} to 500 °C for 24 h, and subsequent cooling at a rate of 1 °C min^{-1} to room temperature.

Spherical particles with an average diameter varying between 10 and 50 nm were prepared by dissociation of iron acetylacetonate and subsequent thermal treatment at 450 °C. The size and shape of the particles were determined by transmission electron microscopy (TEM) measurements performed by a a JEOL 4000 FX, equipped with an ultrathin window (UTW) X-ray detector and operated at 400 kV. The magnetic properties were investigated by means of a commercial superconducting quantum interference device (SQUID) ($H_{max} = 5.5$ T; $4.2\ K < T < 300\ K$) for low-field susceptibility and Mössbauer spectroscopy measurements.

RESULTS AND DISCUSSION

Figures 1 and 2 show TEM micrographs for the as-

Figure 2 TEM micrograph of acicular α-Fe_2O_3 nanoparticles after annealing at 500 °C for 24 h.

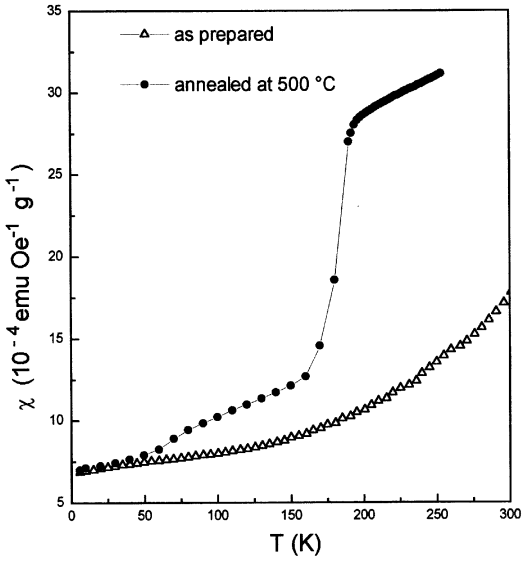

Figure 3 ZFC susceptibility versus temperature for a sample consisting of acicular particles with a major axis of 350 ± 50 nm and a minor axis of 85 ± 5 nm, before and after thermal treatment.

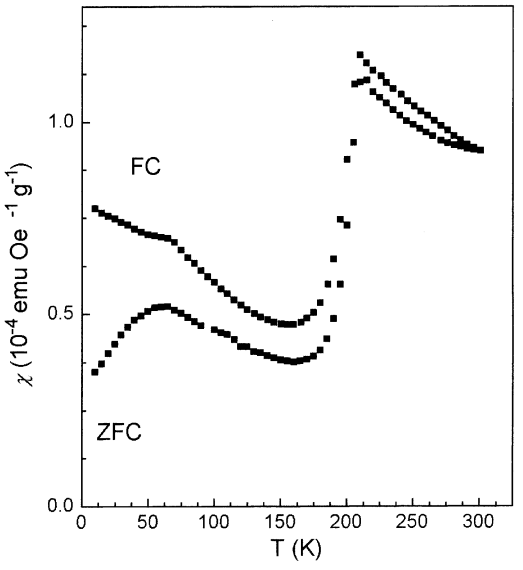

Figure 4 FC and ZFC susceptibility versus temperature for a sample consisting of rhombohedral particles with an average edge of 30 ± 5 nm.

prepared and annealed samples, respectively. The samples consisted of acicular particles with a major axis of 350 ± 50 nm and a minor axis of 85 ± 15 nm. TEM diffraction experiments show the same pattern both before and after the thermal treatment. In particular, each particle produced single-crystal-like diffraction pattern. The structural differences induced by thermal treatment were therefore not related to any change in the crystallographic structure. Low-resolution, out-of-focus TEM observations, capable of putting in contrast any variation in the projected potential of the material on the nanometer scale show that, in the as-prepared state, the particles were constituted of small units separated by a less dense interlayer, while keeping the same crystallographic orientation. The size of the units was of the order of a few nanometers. After thermal treatment the structure appeared to be compacted, probably by a sintering mechanism, and spherical spots a few nanometers wide, randomly distributed in the crystal, were then visible (Fig. 2). In the less dense interlayer region, no spurious elements were detected by X-ray microanalysis performed in the TEM with an energy-dispersive system which was not able to detect X-rays with an energy smaller than 1 kV, typically emitted by the core levels of atoms with atomic number smaller than 11. We guess that the interlayer separating the subunits was constituted of water, the thermal treatment caused its condensation in the form of microdrops that evaporated leaving their imprint as spherical empty spaces in the particle. These structural differences between

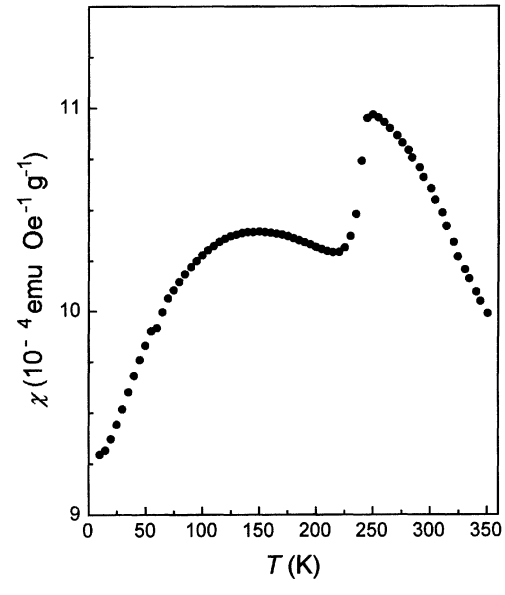

Figure 5 ZFC susceptibility as a function of temperature for a sample consisting of α-Fe_2O_3 spherical particles with an average diameter of 10–50 nm.

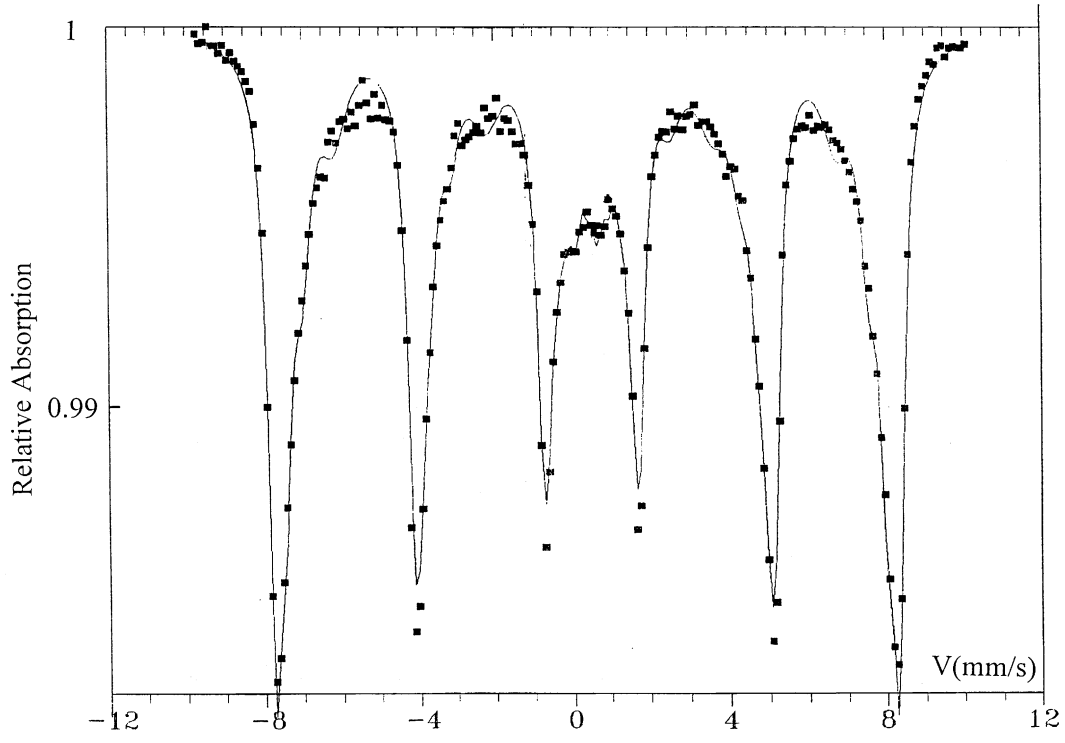

Figure 6 Mössbauer spectrum at room temperature of a sample consisting of α-Fe_2O_3 rhombohedral particles with an average edge of 30 ± 5 nm.

the as-prepared and annealed samples found confirmation in their magnetic behavior (Fig. 3). Before the thermal treatment, the ZFC susceptibilty measured at low field (H = 100 Oe) was observed to increase monotonically with temperature whereas a sharp change in the susceptibilty was observed around 160 K after the annealing treatment, signaling the Morin transition from the antiferromagnetic to the weak ferromagnetic state.

The temperature dependence of the ZFC and FC susceptibility (Fig. 4) of samples consisting of rhombohedral particles (average edge 30 ± 5 nm) gives clear evidence of the Morin transition from a pure antiferromagnet to a weak ferromagnet occurring at $\sim$ 190 K, and of a blocking process revealed by a broad maximum centered at about 60 K. Ac susceptibility measurements performed at various frequencies ($10\,\text{Hz} < \nu < 10^4\,\text{Hz}$) have shown that the Morin temperature does not depend on frequency, indicating that a well-defined phase transition occurs. On the other hand, the temperature of the maximum, related to the average blocking temperature, does depend on the frequency. The same kind of behavior was observed in spherical particles (Fig. 5). A comparison of the results for different samples consisting of particles of different average sizes shows that T_M decreases with decreasing size. Actually, a threshold diameter of approximately 8 nm, below which the Morin transition disappears and superparamagnetic behavior is observed, was found for spherical particles.[16,17]

Moreover, the observation of a broad maximum co-existing with the Morin transition, and a strong increase in the irreversible susceptibility (the difference between the FC and ZFC curves) with decreasing temperature, reflects the existence of a broad distribution of particles. Some particles are very small, below the threshold dimension for the observation of the Morin transition, and show superparamagnetic behavior. Some other particles are bigger, are not superparamagnetic, and show the Morin transition. This is also supported by Mössbauer spectra performed at room temperature (as reported in Fig. 6 for rhombohedral particles with an average edge of 30 nm), which show the co-

existence of a fraction of blocked particles (71.5%) relaxing with $\tau = 10^{-8}$ s (22.5%) and superparamagnetic particles (6%).

CONCLUSIONS

The results show that the magnetic properties of fine α-Fe_2O_3 particles are strongly affected by their internal constitution. The Morin transition was observed in rhombohedral particles at a temperature which decreases with decreasing particle size, whereas in acicular, well-structured particles, constituted by small subunits probably separated by a water interlayer, the Morin transition was observed only after annealing, i.e. after evaporation of water and subsequent compacting of the subunits.

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