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Reversible aggregation and magnetic coupling of α -Fe₂O₃ nanoparticles

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Abstract

The magnetic properties of nanoparticles, including their superparamagnetic relaxation and spin orientation, have been found to depend on the aggregation state due to magnetic exchange coupling being established between surface atoms of neighbouring particles. We show that for samples of α -Fe₂O₃ nanoparticles the agglomeration and the interparticle exchange coupling are reversible processes. Grinding or ultrasonic treatment of aggregated particles can disperse the particles and reduce the magnetic coupling, while drying aqueous suspensions of dispersed particles leads to aggregation and re-establishment of magnetic coupling. The establishment of exchange coupling between neighbouring particles gives evidence for overlapping electronic orbitals of surface atoms of neighbouring particles. This is important not only for understanding the magnetic properties but also for understanding other physical properties e.g. the mechanical properties of dried aggregates. The reversibility (and the decoupling of particles) provides information on the strength of the coupling.

1. Introduction

Recent studies have shown that the aggregation state plays a decisive role for the physical properties of nanoparticles [1–18]. For instance, 3 nm particles of ZnS have been found to show a less strained/disordered crystal structure with increasing aggregation [5]. In studies of magnetic nanoparticles it has been demonstrated that aggregation or inter-particle interactions can have a significant influence on the magnetic properties [6–18]. Mössbauer spectroscopy of nanoparticles of antiferromagnetic materials such as α -Fe₂O₃ has shown that aggregation of particles from aqueous suspensions can result in a significant suppression of the superparamagnetic relaxation, and because magnetic dipole interactions are too weak to account for the effect it has been concluded that exchange coupling between surface atoms of neighbouring nanoparticles is responsible for this phenomenon [6–11]. Mössbauer studies of the magnetic structure of α -Fe₂O₃ nanoparticles have also shown that exchange interactions

between aggregated particles with different crystalline orientations can be significant and change the sublattice magnetization directions [12]. In the present work we have used Mössbauer spectroscopy to show that the aggregation and magnetic coupling of uncoated α -Fe₂O₃ nanoparticles are reversible processes, i.e. the aggregated particles, dried from suspension, can be re-dispersed and magnetically decoupled by gentle grinding or by ultrasonic agitation, but the aggregation and magnetic coupling can be re-established by subsequent drying of the aqueous suspensions.

2. Experimental details

α -Fe₂O₃ nanoparticles were prepared by a gel–sol method similar to that described by Sugimoto *et al* [19]. After washing, the particles were left in aqueous suspension for about a week and then freeze-dried. This dry sample is referred to as the as-prepared sample, and it is from the same batch as that described in [11]. Transmission electron microscopy [11] has shown that the particles have rounded shapes with particle size typically in the range of 5–10 nm, in accordance with the results of x-ray and neutron diffraction measurements, which yielded a particle size of about 7 nm [11].

Part of the as-prepared sample of α -Fe₂O₃ particles was ground for two days together with non-magnetic nanoparticles of amorphous SiO₂ (weight ratio 1:3) in air in an agate ball mill. The mill rotated gently, 40 times min⁻¹. The weight ratio between balls and sample was 15:1. No chemical reaction during grinding could be detected by Mössbauer spectroscopy and x-ray diffraction [11].

We also exposed a suspension of the as-prepared sample to ultrasound for up to 6 h, either in a bath of type Branson 2510 or by immersion of a horn into the suspension, in order to disperse the particles.

Parts of the sample, treated by ultrasonic horn for 6 h, were subsequently freeze-dried or dried by evaporation.

Mössbauer spectra were obtained using conventional constant acceleration Mössbauer spectrometers with sources of ⁵⁷Co in rhodium. Low-temperature spectra were obtained using a temperature-controlled liquid nitrogen cryostat. The spectrometers were calibrated with a 12.5 μ m α -Fe foil at room temperature.

3. Results

3.1. Grinding

Previous studies have shown that grinding of nanoparticles by hand in a mortar or by low-energy ball-milling can dramatically reduce the inter-particle interactions [10]. The effect of separation of the particles by grinding is illustrated by the Mössbauer spectra shown in figure 1. Figures 1(a) and (b) show room-temperature and 180 K Mössbauer spectra of the as-prepared sample, and figures 1(c) and (d) show room temperature and 180 K spectra of the ground sample. The spectra of the as-prepared sample consist of a sextet with substantially broadened lines at 180 K and even more at 295 K. These spectra are different from those of isolated α -Fe₂O₃ nanoparticles, which show a sextet with narrow lines collapsing to a doublet with narrow lines around the superparamagnetic blocking temperature [6, 8, 9], typically below 100 K for α -Fe₂O₃ particles with sizes of the order of 7 nm [20]. The spectral behaviour of the as-prepared sample in figures 1(a) and (b) is typical for samples of interacting nanoparticles in which superparamagnetic relaxation is suppressed [6–10]. In contrast, the spectra of the ground sample (figures 1(c) and (d)) consist only of a doublet, indicating that all particles exhibit fast superparamagnetic relaxation. The doublet dominates down to \sim 60 K. This shows that the

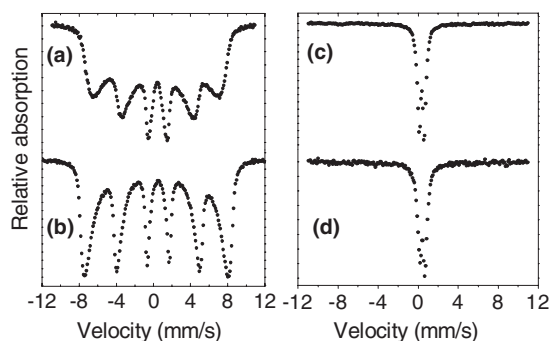


Figure 1. Mössbauer spectra of α -Fe₂O₃ nanoparticles. The as-prepared sample at (a) room temperature and (b) 180 K. The sample after grinding at (c) room temperature and (d) 180 K.

grinding has led to particle separation and a significant reduction of the interactions. The effect is not due to a reduction of the particle size, as it has been shown that the particle size rather increases than decreases during grinding of ~ 10 nm α -Fe₂O₃ nanoparticles [10].

3.2. Ultrasonic treatments and reversibility

As a different method for separating the particles, part of the as-prepared sample was suspended in water (50 mg per 80 ml), and then treated with ultrasound of increasing intensity and duration. After the ultrasonic treatments, parts of the suspension were transferred to 1 ml sample holders for Mössbauer spectroscopy and frozen by immersion in liquid nitrogen. Mössbauer spectra at 180 K, shown in figures 2(a)–(c), reveal a clear tendency of faster relaxation with increasing intensity and duration of the ultrasonic treatment. If the sample is suspended in water and treated for 15 min in an ultrasonic bath, then its spectrum (figure 2(a)) is very similar to that of the untreated sample (figure 1(b)). Thus, neither the suspension in water nor the ultrasonic bath treatment affects the inter-particle interactions significantly. However, application of a more intense treatment of the sample by immersing an ultrasonic horn into the suspension for 15 min led to a faster superparamagnetic relaxation of the particles, seen as the appearance of a doublet in the spectrum (figure 2(b)). Using the horn for 6 h (and keeping the suspension cold by a surrounding, ice-cooled water bath) led to an even faster relaxation of the particles. After this treatment the Mössbauer spectrum (figure 2(c)) consists solely of a doublet. The results of figures 2(a)–(c) show that, like grinding, intense and durable ultrasonic treatments can dramatically reduce the inter-particle exchange interactions.

In order to investigate if the effects of interactions could be re-established after ultrasonic treatment, we studied the influence of drying the suspensions of re-dispersed nanoparticles. A part of the sample, which had been ultrasonically treated with the horn for 6 h, was subsequently dried at room temperature over a couple of days and a Mössbauer spectrum was obtained at 180 K (figure 2(d)). This spectrum is qualitatively very similar to that of the as-prepared sample (figure 1(b)), although the lines are slightly broader. This shows that during the drying of the ultrasonically treated sample, the particles again aggregate and re-establish inter-particle exchange coupling.

3.3. Influence of the duration of the drying

Since the coupling between the particles seems to be established during drying, we also investigated the influence of the drying procedure. Figure 3 shows room temperature Mössbauer spectra of samples, which after exposure to intense ultrasonic treatment by use

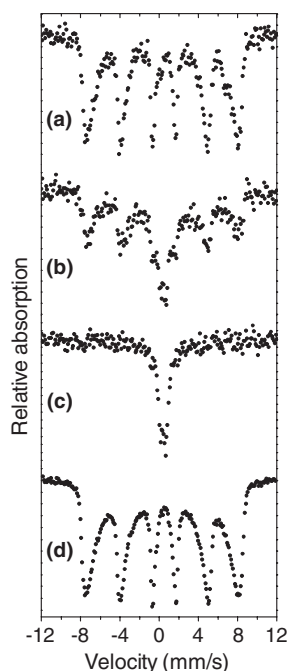


Figure 2. (a)–(c) Mössbauer spectra of frozen suspension of α - Fe_2O_3 nanoparticles obtained at 180 K. (a) After 15 min of ultrasonic treatment in a bath. (b) After 15 min treatment by the horn. (c) After 6 h treatment by the horn. (d) Spectrum after drying sample material, which was treated with ultrasound for 6 h by the horn.

of the horn for 6 h were dried with increasing duration. If the suspensions were frozen immediately after the ultrasonic treatment and then freeze-dried, the particles show less interaction (a sextet is absent in the spectrum in figure 3(a)) than after drying the suspended particles under ambient conditions in an open Petri dish over a couple of days (figure 3(b)). If the suspensions were dried at ambient conditions, but under a perforated lid over a couple of weeks, the area of the sextet increases at the expense of the central doublet, showing that the particles achieve even stronger interaction (figure 3(c)), presumably due to a denser aggregation. Thus, drying the particles from suspension with increasing duration of the drying process leads to increasing aggregation and coupling between the particles.

We note that the suppression of the superparamagnetic relaxation is not quite as strong in figure 3 as in the as-prepared sample (figure 1(a)), but it is likely that this can be explained by differences in the time the particles were left in solution before drying. The sample in figure 3(a) was frozen immediately after ultrasonic treatment, while for the as-prepared sample the particles were left in suspension for about a week before the particles were freeze-dried, leaving time for the particles to aggregate. Moreover, differences in concentration of particles during drying may also play a role for the differences in aggregation between the as-prepared and the treated samples. In the as-prepared sample about 15 g was dried in 1000 ml water, while for the treated samples (figure 3) it was only about 50 mg per 100 ml water.

4. Discussion

The results show that aggregation or dispersion of 7 nm α - Fe_2O_3 particles is followed by an increase or decrease in magnetic coupling, respectively. It is interesting that Huang *et al* [5]

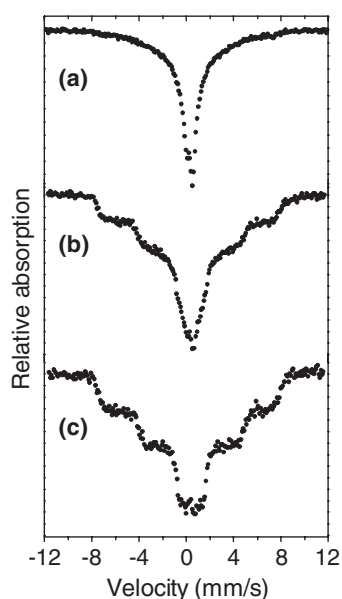


Figure 3. Mössbauer spectra obtained at room temperature of samples dried with increasing duration from aqueous suspension after 6 h of ultrasonic treatment. (a) Freeze-dried. (b) Dried at ambient conditions over a couple of days. (c) Dried at ambient conditions over a couple of weeks.

have found that by using similar processes (ultrasonic treatment and drying) it is possible to reversibly switch between ordered and disordered crystal structures of 3 nm ZnS particles. Both studies clearly show that the fundamental physical properties of nanoparticles such as structure and magnetic properties are extremely dependent on the nanoparticles' state of aggregation.

Since the established exchange couplings between α -Fe₂O₃ nanoparticles are short-range interactions, our results show that overlap of electronic orbitals is achieved between surface atoms of aggregated neighbouring particles. Some kind of chemical bonds between surface atoms of nanoparticles will have implications for the mechanical coupling of both magnetic and non-magnetic nanoparticles, and may explain why dried suspensions often form solid agglomerates. This can be important for the understanding of, for example, the mechanical properties of dry sediments in nature.

The reversibility provides qualitative information on the strength of the coupling between the particles: the coupling is strong enough that it can influence the properties of the particles, but weak enough that ultrasonic treatment or gentle grinding can act to separate the particles.

The exact nature of the coupling mechanisms as well as the type of bonding between particles is not yet fully understood, but it would be interesting to study and quantify further because it seems to govern both the magnetic and the mechanical properties of aggregates. Previous studies have shown that oriented attachment (epitaxial assembly of nanoparticles) may occur, e.g., between TiO₂ nanoparticles aggregated at elevated temperatures and pressures [1, 2], or between α -Fe₂O₃ nanoparticles synthesized by a gel-sol method [11]. In the case of oriented attachment, the bonding strength can be expected to be strong, i.e. similar to that inside the particles. Particles which are randomly aggregated or aggregated with a layer of adsorbed water between them are expected to show a weaker magnetic or mechanical coupling.

5. Conclusions

The present investigations have shown that magnetic coupling between α -Fe₂O₃ nanoparticles can be established both during drying of freshly prepared particles and during drying of aqueous suspensions of re-dispersed particles. It can therefore be concluded that it can be a reversible phenomenon. We suggest that the magnetic coupling between nanoparticles is accompanied by a mechanical coupling, and that this may explain some of the mechanical properties of dried suspensions of powders.

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