Spin Rotation in α-Fe_2O_3 Nanoparticles by Interparticle Interactions

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Nanoparticles of α-Fe_2O_3 (hematite) typically have the sublattice magnetization directions in the hexagonal (001) plane below the Néel temperature. By use of Mössbauer spectroscopy we have found that for agglomerated particles the sublattice magnetization may be rotated of the order of 15° out of plane, depending on the particle size. The spin rotation can be explained by exchange interaction between neighboring particles with nonparallel (001) planes. The results imply that interparticle interactions can lead to spin directions deviating from the easy axis defined by the magnetic anisotropy.

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It is well established that the properties of magnetic nanoparticles differ significantly from the bulk properties [1]. It is particularly interesting that the basic properties of magnetic materials, such as the magnetic structure, can be different for nanoparticles and bulk materials. For example, due to surface effects, nanoparticles of antiferromagnetic NiO may have a complicated eight-sublattice magnetic structure [2]. In α-Fe_2O_3 nanoparticles, the magnetic phase transition, the Morin transition, is suppressed [3,4], and the spin-flop field decreases with decreasing particle size [5]. In ferrimagnetic nanoparticles the lower symmetry of surface atoms and defects in the interior can lead to spin canting [6–8]. Recent studies have shown that the magnetic properties of nanoparticles, in addition to differing from bulk magnetic properties, are extremely sensitive to interparticle interactions [9–20]. Strong magnetic dipole interactions between nanoparticles of ferromagnetic or ferrimagnetic materials have been found to suppress the superparamagnetic relaxation [9,10] and may result in spin-glasslike ordered states of the particles at low temperatures [11–14]. It has also been shown that exchange coupling between nanoparticles can significantly affect superparamagnetic relaxation [15–17] and coercivity [18–20] as well as induce exchange bias [19]. In nanocrystalline hard magnetic materials, the remanent magnetization can be enhanced because the exchange coupling between neighboring grains to some extent may align the magnetization directions [21–23]. In nanocrystalline soft magnetic materials, a similar mechanism can result in superior soft magnetic properties [24]. However, up to now it has not been generally considered that the sublattice magnetization direction in antiferromagnetic nanoparticles could be influenced by interactions. We have addressed the question of a possible influence of interparticle interactions on an antiferromagnetic structure by studying interacting nanoparticles of α-Fe_2O_3 by Mössbauer spectroscopy.

The crystal structure of α-Fe_2O_3 can be described in terms of alternating iron and oxygen layers stacked along the [001] axis of the hexagonal unit cell [25]. The Fe layers order antiferromagnetically below the Néel temperature (955 K in bulk), such that the magnetization directions of neighboring Fe layers are antiparallel [25]. Between the Néel temperature and the Morin temperature, $T_M \approx 263$ K in bulk, the sublattice magnetization directions in α-Fe_2O_3 are confined by magnetic anisotropy to lie in the (001) plane. Below the Morin transition temperature the sublattice magnetization directions are parallel to the [001] axis. For particles of α-Fe_2O_3 with diameters less than ~20 nm, the Morin transition is reported absent [3,4,25].

The angle θ between the sublattice magnetization directions and the [001] axis of α-Fe_2O_3 can be deduced from the quadrupole shift, ε, of the magnetically split Mössbauer spectra. In α-Fe_2O_3 the electric field gradient is parallel to the [001] axis and the quadrupole shift is given by

$$\varepsilon = \varepsilon_0(3\cos^2\theta - 1)/2, \tag{1}$$

where $\varepsilon_0 = 0.200$ mm/s [25]. Thus, when the sublattice magnetization of α-Fe_2O_3 nanoparticles is in the (001) plane, $\varepsilon = -0.100$ mm/s. Here we report that agglomerated nanoparticles of α-Fe_2O_3 can have quadrupole shifts deviating distinctly from -0.100 mm/s, indicating an out-of-plane sublattice magnetization due to interparticle exchange interactions.

Powder samples of 6 nm α-Fe_2O_3 particles were prepared by thermal decomposition of $Fe(NO_3)_3 \cdot 9H_2O$ [4], 8, 9, 11, 12, and 13.5 nm particles by means of gel-sol methods similar to those described by Sugimoto *et al.* [4,16,26], and 20 nm particles by forced hydrolysis [15]. After preparation, the particles were dried from aqueous suspensions. In order to prepare reference samples, in which the particles were not in contact with one another, particles in part of the samples were coated with phosphate (the 8 nm particles) or with oleic acid before drying. Uncoated, dried 9 nm particles were separated by low-energy balling with particles of SiO_2 [27,28]. The samples were characterized by x-ray diffraction and transmission electron microscopy, which revealed crystalline, pseudospherical particles with some size distribution [4,15,16,27]

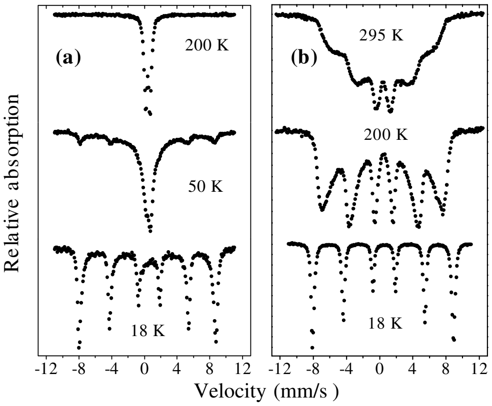

FIG. 1. Mössbauer spectra obtained at the indicated temperatures of (a) coated and (b) uncoated 8 nm α-Fe_2O_3 particles.

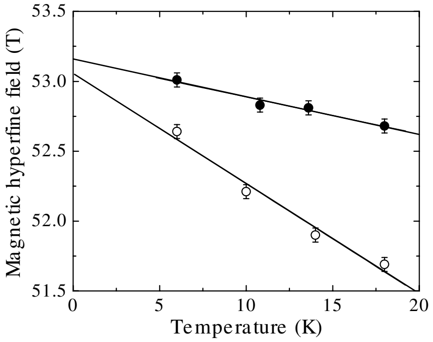

FIG. 2. The magnetic hyperfine field, B_{hf}, of coated (open circles) and uncoated (solid circles) 8 nm α-Fe_2O_3 particles found from Mössbauer spectra obtained at low temperatures. The lines are linear fits to the data extrapolated down to 0 K.

and with lattice constants close to the bulk value for α-Fe_2O_3.

The samples of coated particles show typical superparamagnetic relaxation behavior, while in the samples of uncoated particles the relaxation is largely suppressed due to exchange interaction between the particles [15,16]. For α-Fe_2O_3 nanoparticles, dipole interactions are too small to explain the effects on relaxation [15,16]. For illustration of the influence of interaction on relaxation, Fig. 1 shows Mössbauer spectra of coated and uncoated 8 nm α-Fe_2O_3 particles. The coated particles show superparamagnetic relaxation with a blocking temperature of about 40 K (i.e., 50% of the sextet has collapsed to a central doublet at this temperature), while for the agglomerated uncoated particles the superparamagnetic relaxation is suppressed (i.e., only the sextet exists at least up to room temperature, but it broadens and the average hyperfine field diminishes in a way typical for interacting magnetic nanoparticles [10,15,16]). At low temperatures, the hyperfine field for the noninteracting particles decreases faster with temperature than the hyperfine field of interacting particles (Fig. 2), in accordance with the expected influence of interactions on collective magnetic excitations [15,29].

The quadrupole shift of the sextet in the Mössbauer spectra of noninteracting particles, obtained at low temperature, is close to the bulk value above the Morin transition temperature, $\varepsilon \approx -0.100$ mm/s. However, the absolute value of ε was smaller for the interacting samples. For example, for the 8 and 9 nm particles, $\varepsilon = -0.075$ and -0.087 mm/s, respectively. The uncertainty of the values of ε is ± 0.0035 mm/s. Thus, the values of ε for the interacting nanoparticles are, beyond uncertainty, different from the values for noninteracting particles. This is illustrated in Fig. 3(a), which shows the quadrupole shifts for interacting and noninteracting 8 nm particles at temperatures between 6 and 25 K. Figure 3(a) also shows that at low temperatures, where essentially all particles are below the blocking temperature, the quadrupole shift is, within experimental uncertainty, independent of temperature for both interacting and noninteracting particles. This was seen also at higher temperatures for samples where all particles were below their blocking temperature.

Figure 3(b) shows the quadrupole shift at 20 K for a number of different samples of interacting particles as a function of particle size. These data show that there is an overall tendency that the smaller the interacting particles are, the more ε deviates from the bulk value of -0.100 mm/s. Variations in ε, beyond the general trend, could be caused by different strengths of interactions between the particles, which can depend on, e.g., sample preparation and the duration of the drying process [28].

The interparticle interaction between the α-Fe_2O_3 particles can be reduced by gently ball milling the samples with nonmagnetic nanoparticles [27], leading to a faster relaxation. Accordingly, we have found that grinding of the

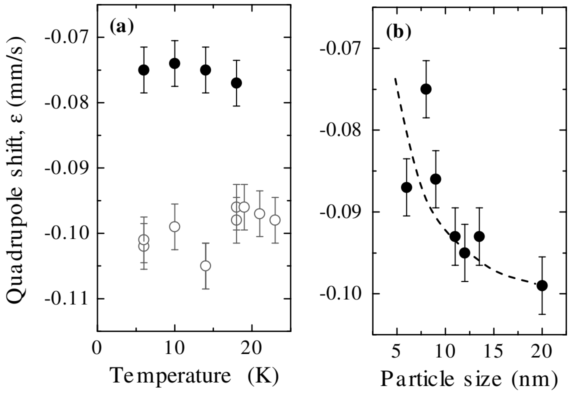

FIG. 3. (a) The quadrupole shift, ε, of coated (open circles) and uncoated (solid circles) 8 nm α-Fe_2O_3 particles found from Mössbauer spectra obtained at low temperatures. (b) The quadrupole shifts, ε, found for uncoated samples of α-Fe_2O_3 nanoparticles of different particle sizes. The dashed line is a guide to the eye.

interacting 9 nm α-Fe_2O_3 particles changed the quadrupole shift of the sample from -0.087 to -0.094 mm/s (determined at 20 K). The Mössbauer spectra of the ground sample show a sextet relaxing to a doublet with a blocking temperature of about 60 K. In a temperature range close to the blocking temperature, the six-line component coexists with a central doublet. We have measured the quadrupole shifts of the sextet as a function of temperature in this range. The results, which are shown in Fig. 4, indicate that the quadrupole shift of the remaining sextet increases with temperature. This suggests that the more weakly interacting particles in the sample relax faster, while the particles with stronger interparticle interactions have a slower relaxation.

Deviations from the ε value of -0.100 mm/s, as found for the samples of the interacting particles, suggest an out-of-plane sublattice magnetization. The values of θ, estimated from Eq. (1) for the interacting 8 and 9 nm particles, are 72° and 77°, respectively, and for the ground 9 nm particles it is 82°. Since spin rotation is observed only in the samples of interacting particles, and since it can be diminished by reducing the interparticle interactions, its origin seems to be interparticle exchange interactions in these samples. It has recently been found that α-Fe_2O_3 nanoparticles often are in direct contact and may assemble preferably with common [001] axes [28]. An out-of-plane rotation of spins is, however, expected to be prevalent only when [001] axes of neighboring particles are nonparallel. Localized spin canting at the surface of the particles [6–8] may also contribute to the size and direction of the effective interaction field. The strong suppression of the superparamagnetic relaxation in the samples of agglomerated particles is presumably due to exchange interactions between a large network of particles with both parallel and nonparallel [001] directions.

The sublattice magnetization directions, derived from the quadrupole shifts, are averages for the ensembles of particles. In a sample, where the particles are randomly agglomerated, some particles may show larger out-of-plane rotations, some smaller ones. Since the particles are too small to form magnetic domains, it is expected that the out-of-plane rotations occur more or less coherently within each particle. In principle, a distribution in angles will give rise to a broadening of the Mössbauer lines. However, we have estimated that a distribution in the range 0°–30° gives a negligible broadening.

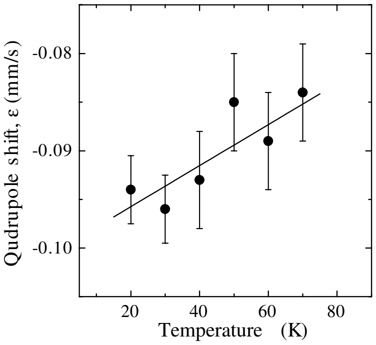

FIG. 4. The quadrupole shifts, ε, of 9 nm α-Fe_2O_3 particles after grinding with SiO_2 nanoparticles, found from Mössbauer spectra obtained at temperatures between 20 and 70 K. The solid line is a linear fit to the data.

A Morin transition in some of the interacting particles cannot explain the deviation in ε from -0.100 mm/s, since a Morin transition in part of a sample would give rise to an asymmetry in the spectra such that, for example, line no. 6 is broader and less intense than line no. 1 [16], but this was not observed here. Moreover, if a Morin transition were present, one might expect it to be most pronounced in the samples with the largest particles. Instead, the smallest particles show the largest out-of-plane rotation of their sublattice magnetization, suggesting that the smallest particles, which have the smallest anisotropy energy, most easily have their sublattice magnetization rotated out of the plane.

Neglecting the small in-plane anisotropy, the magnetic energy of an α-Fe_2O_3 nanoparticle in close contact with its neighbors may be written

$$E = K_1 V \sin^2\theta - E_{\mathrm{int}} \cos(\theta - \theta_0), \qquad (2)$$

where K_1 (<0) is the out-of-plane magnetic anisotropy energy constant, V is the volume, E_{int} is the net interaction energy due to exchange coupling between particles, and $\theta - \theta_0$ represents the angle between the sublattice magnetization direction and the interaction field. We consider for simplicity the case where $\theta_0 = 0°$ and find for small E_{int} that the sublattice magnetization direction is given by

$$\cos\theta = -E_{\mathrm{int}}/(2K_1 V). \qquad (3)$$

This seems to be qualitatively in accordance with the size dependence of the quadrupole shift, shown in Fig. 3(b), but since the magnetic anisotropy constants of nanoparticles may increase with decreasing particle size [30,31], the size dependence of ε may be smaller than Eq. (3) might suggest. The value of K_1 in α-Fe_2O_3 nanoparticles is of the order of -10^4–-10^5 J/m^3 [4]. Assuming that $K_1 = -5 \times 10^4$ J/m^3 for 9 nm particles, for which $\varepsilon \approx -0.085$ mm/s, we find that $E_{\mathrm{int}} \approx 8 \times 10^{-21}$ J, corresponding to a temperature of about 600 K. As discussed elsewhere [15,29], the value of E_{int} can be estimated from the temperature dependence of the hyperfine fields of interacting and noninteracting particles. Using the data of Fig. 2, we find that $E_{\mathrm{int}}/k_B \approx 1300$ K, which is in reasonable agreement with the estimate made above. This strongly supports our conclusion that the rotation of the sublattice magnetization is due to interparticle interactions.

The magnetic hyperfine field, B_{hf}, at an iron nucleus has a contribution from the magnetic dipole fields from the surrounding magnetic ions. When the sublattice magnetization of α-Fe_2O_3 rotates out of the (001) plane, the dipole field changes. Tobler *et al.* [32] calculated the magnetic dipole field as a function of the angle between the sublattice magnetization direction and the [001] direction and found that this could explain the change in B_{hf} of 0.8 T observed at the Morin transition. According to the calculations, the dipole field is given by

$$B_{\mathrm{dip}} = (1\text{–}3\cos^2\theta) \times 0.325\ \mathrm{T}. \tag{4}$$

From this expression, we find that an 18° rotation out of the plane, as we have found for the 8 nm particles, should result in an increase in B_{hf} of 0.11 T. By extrapolation of the data of Fig. 2 to 0 K, we find that B_{hf} at 0 K for the interacting particles is 0.09 (± 0.06) T larger than the value for the noninteracting particles, in reasonable agreement with the calculated value. This supports our conclusion that the sublattice magnetization is oriented out of plane in the samples of interacting particles.

The present study shows that interparticle exchange interaction between antiferromagnetic nanoparticles is a mechanism that can lead to rotation of the sublattice magnetization away from the direction defined by the magnetic anisotropy. This result stresses that the magnetic properties of nanoparticles cannot solely be described by considering individual particles, but they have to be understood in terms of interactions, too. An influence of exchange interaction, as deduced from a suppression of superparamagnetic relaxation by Mössbauer spectroscopy, has been found also in agglomerated NiO nanoparticles [17] as well as in composites containing antiferromagnetic nanoparticles of different materials [16]. It is therefore likely that the rotation of sublattice magnetization is prevalent also in other systems of antiferromagnetic nanoparticles.

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[1] J. L. Dormann, D. Fiorani, and E. Tronc, Adv. Chem. Phys. **98**, 283 (1997).
[2] R. H. Kodama, S. A. Makhlouf, and A. E. Berkowitz, Phys. Rev. Lett. **79**, 1393 (1997).
[3] W. Kündig, K. J. Ando, G. Constabaris, and R. H. Lindquist, Phys. Rev. **142**, 327 (1966).
[4] F. Bødker and S. Mørup, Europhys. Lett. **52**, 217 (2000).
[5] R. D. Zysler *et al.*, Phys. Rev. B **68**, 212408 (2003).
[6] J. M. D. Coey, Phys. Rev. Lett. **27**, 1140 (1971).
[7] A. H. Morrish and K. Haneda, J. Magn. Magn. Mater. **35**, 105 (1983).
[8] S. Mørup, J. Magn. Magn. Mater. **266**, 110 (2003).
[9] W. Luo, S. R. Nagel, T. F. Rosenbaum, and R. E. Rosensweig, Phys. Rev. Lett. **67**, 2721 (1991).
[10] S. Mørup, F. Bødker, P. V. Hendriksen, and S. Linderoth, Phys. Rev. B **52**, 287 (1995).
[11] C. Djurberg *et al.*, Phys. Rev. Lett. **79**, 5154 (1997).
[12] H. Mamiya, I. Nakatani, and T. Furubayashi, Phys. Rev. Lett. **80**, 177 (1998).
[13] T. Jonsson, P. Svedlindh, and M. F. Hansen, Phys. Rev. Lett. **81**, 3976 (1998).
[14] Y. Sun, M. B. Salamon, K. Garnier, and R. S. Averback, Phys. Rev. Lett. **91**, 167206 (2003).
[15] M. F. Hansen, C. B. Koch, and S. Mørup, Phys. Rev. B, **62**, 1124 (2000).
[16] C. Frandsen and S. Mørup, J. Magn. Magn. Mater. **266**, 36 (2003).
[17] F. Bødker, M. F. Hansen, C. B. Koch, and S. Mørup, J. Magn. Magn. Mater. **221**, 32 (2000).
[18] H. Zeng *et al.*, Nature (London) **420**, 395 (2002).
[19] J. Sort *et al.*, Appl. Phys. Lett. **75**, 3177 (1999); J. Sort *et al.*, J. Magn. Magn. Mater. **219**, 53 (2000).
[20] C. Frandsen *et al.*, Phys. Rev. B **70**, 134416 (2004).
[21] R. W. McCallum, A. M. Kadin, G. B. Clemente, and J. E. Keem, J. Appl. Phys. **61**, 3577 (1987).
[22] A. Manef, R. A. Buckley, H. A. Davies, and M. Leonowicz, J. Magn. Magn. Mater. **101**, 360 (1991).
[23] H. Kronmüller, Nanostruct. Mater. **6**, 157 (1995).
[24] G. Herzer, Scr. Metall. Mater. **33**, 1741 (1995); J. Magn. Magn. Mater. **157**, 133 (1996).
[25] A. H. Morrish, *Canted Antiferromagnetism: Hematite* (World Scientific, Singapore, 1994).
[26] T. Sugimoto, Y. Wang, H. Itoh, and A. Muramatsu, Colloids Surf. A **134**, 265 (1998).
[27] M. Xu, C. R. H. Bahl, C. Frandsen, and S. Mørup, J. Colloid Interface Sci. **279**, 132 (2004).
[28] C. Frandsen *et al.* (to be published).
[29] S. Mørup, J. Magn. Magn. Mater. **37**, 39 (1983).
[30] F. Bødker, S. Mørup, and S. Linderoth, Phys. Rev. Lett. **72**, 282 (1994).
[31] E. Tronc, Nuovo Cimento Soc. Ital. Fis. **18D**, 163 (1996).
[32] L. Tobler, W. Kündig, and I. Savic, Hyperfine Interact. **10**, 1017 (1981).