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Characterisation of iron oxide nanoparticles by Mössbauer spectroscopy at ambient temperature

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ABSTRACT

Magnetite (Fe_3O_4) nanoparticles are important as contrast agents in magnetic resonance imaging or for magnetic drug targeting. Such particles can be made by different ways of synthesis, but depending on their size they tend to oxidise to maghemite (γ-Fe_2O_3), which is often less desirable because of its lower magnetisation. Mössbauer spectroscopy is well suited for determining the relative amounts of the two iron oxides in a sample. When measured at 4.2 K the nanoparticles typically exhibit well-defined but complicated hyperfine spectra that may present some problems of evaluation, but eventually yield reliable results for the degree of oxdation. At room temperature, however, particles smaller than about 15 nm are affected by superparamagnetic relaxation, which renders Mössbauer spectroscopy useless for their characterisation. To characterise magnetic nanoparticles even at room temperature, we designed an arrangement of permanent magnets to apply an external magnetic field of about 0.7 T to the Mössbauer absorbers. This has been found to be sufficient to give rise to magnetically split Mössbauer spectra that allow a distinction between magnetite and maghemite and to determine their relative amounts in a sample.

1. Introduction

The characterisation of magnetic iron oxide nanoparticles is important for their use as contrast agents in magnetic resonance imaging and as carriers for magnetic drug targeting [1–6]. Such particles can consist of magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), or a mixture of both. Because of its higher magnetisation ($92\ A\ m^2\ kg^{-1}$) magnetite is preferred to maghemite for many applications [7]. Mössbauer spectroscopy can be used to characterise iron oxides because the magnetic hyperfine patterns are different for the various types of iron oxides. Magnetite and maghemite both have a spinel structure and show a strong Zeeman splitting even at ambient temperature because of their ferrimagnetic order [8]. In maghemite, the Mössbauer parameters of Fe(III) on the tetrahedral (A) and octahedral (B) sites are very similar and hardly distinguishable in the Mössbauer spectra [9]. In magnetite, however, the B-sites are occupied by equal amounts of Fe(II) and Fe(III). Above the Verwey transition temperature ($T_V = 119$ K) [10], electron hopping between the ions on the B-sites occurs and leads to an effective valence state of Fe(2.5). Therefore, in the Mössbauer spectra the B-sites yield only one magnetically split sextet, with a smaller hyperfine field than the Fe(III) on the A-sites and an isomer shift intermediate between that of Fe(III) and Fe(II). Hence, the magnetite spectrum consists of two sextets, one for the Fe(III) ions on the tetrahedral sites and one for the mixed-valence Fe(2.5) ions on the octahedral sites [11–13]. For pure magnetite the relative amount of the A- and the B-components is 1:2. Below the Verwey transition temperature, the electrons on the B-sites become localised, which facilitates a distinction of the Fe(II) and Fe (III) lattice sites [14,15]. For a mixture of magnetite and maghemite or for partially oxidised magnetite, the Mössbauer parameters stay essentially the same and only the relative intensities of the sextets change. By fitting such spectra, one can determine the relative amounts of magnetite and maghemite or the degree of oxidation of magnetite. Thus, bulk magnetite and maghemite can be distinguished from each other rather easily by room temperature Mössbauer spectroscopy [16,17].

Unfortunately, this is not generally true for iron oxide nanoparticles, for which the magnetic hyperfine splitting may collapse because of their superparamagnetic relaxation [18,19]. Since the magnetisation of the particles changes direction rapidly, the magnetic hyperfine splitting either collapses completely or the hyperfine patterns are so severely broadened that the distinction between different oxidation states becomes impossible. For uniaxial magnetic anisotropy, the magnetisation flips with a time

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constant given by the Néel relaxation time [20]

$$\tau = \tau_0 \exp\left(\frac{KV}{k_B T}\right). \tag{1}$$

Here, τ_0 is of the order of $10^{-13} - 10^{-9}$ s, K is the magnetic anisotropy constant, V is the particle volume, k_B is Boltzmann's constant and T is the absolute temperature. This relaxation severely affects the temperature and particle size dependence of the Mössbauer spectra [21–23]. If the relaxation time falls below the timescale of Mössbauer spectroscopy ($\approx 10^{-9}$ s), the hyperfine spectrum broadens and eventually collapses completely, like for paramagnetic substances. With increasing relaxation time, the Mössbauer pattern broadens, then an initially broad sextet will appear and become more prominent and sharp. By means of quantum mechanics the line shapes of such spectra in the transition region can be calculated [24]. At ambient temperature, magnetite and maghemite exhibit well-defined magnetic hyperfine splitting only for particles with a diameter larger than about 15 nm, for smaller ones low temperatures are required to slow down the superparamagnetic relaxation [13,25–27]. Therefore, Mössbauer spectra of partially oxidised magnetite nanoparticles measured at 4.2 K, where the relaxation is certainly blocked, appear to be the only possibility for a characterisation despite difficulties in their evaluation [28].

However, even when superparamagnetic relaxation is fast, a well-defined magnetic hyperfine splitting can be obtained by applying an external magnetic field, $\mathbf{B}_{\mathbf{app}}$, which magnetises the nanoparticles [29–32]. The effective hyperfine splitting is then proportional to the total magnetic field at the nucleus

$$\mathbf{B}_{\mathbf{tot}} = \mathbf{B}_{\mathbf{ind}} + \mathbf{B}_{\mathbf{app}} \tag{2}$$

where $\mathbf{B}_{\mathbf{ind}}$ is the induced hyperfine field [22]. Above the blocking temperature, it is approximately given by the Langevin function:

$$\mathbf{B}_{\mathbf{ind}} = \mathbf{B}_{\mathbf{0}} L\left(\frac{M_S V B_{app}}{k_B T}\right) \tag{3}$$

where $\mathbf{B}_{\mathbf{0}}$ is the hyperfine field that would be observed for slow superparamagnetic relaxation and M_S is the saturation magnetisation of the magnetic particle [22]. For ferrimagnetic substances like magnetite or maghemite that has a high saturation magnetisation, the Langevin function saturates quickly which results in a significant hyperfine splitting for superparamagnetic iron oxide particles at ambient temperature even for applied fields less than 1 T [33]. The angle between the total magnetic field at the nucleus and the propagation direction of the gamma rays strongly influences the relative areas of the six lines in the Mössbauer spectrum [22]. The relative intensities of the six lines on this angle are given by 3: x: 1: 1: x: 3 with

$$x = \frac{4\sin^2\theta}{2 - \sin^2\theta} \tag{4}$$

where θ is the angle between the total magnetic field and the propagation direction of the gamma rays. If the sample is magnetised perpendicular to the gamma ray direction, the area ratio of the six lines is 3: 4: 1: 1: 4: 3. Since magnetite and maghemite have a ferrimagnetic order, the hyperfine field at the A-sites will be parallel and the hyperfine field at the B-sites anti-parallel to the applied field. This results in an increased magnetic hyperfine splitting for the A-sites and a reduced splitting for the B-sites. If the applied field is sufficiently strong, the tetrahedral and octahedral Fe(III) components in maghemite can be distinguished [34]. A comprehensive theoretical description of the influence of an external magnetic field on the Mössbauer spectrum of superparamagnetic nanoparticles requires a sophisticated quantum mechanical approach [35–37].

In the following, we describe the construction of a magnet using NdFeB permanent magnets in a Halbach array to obtain a magnetic field at the Mössbauer absorber that is sufficient to yield magnetically split spectra of magnetite/maghemite nanoparticles at ambient temperature. In this way, it is possible to distinguish between the two iron oxides in particles with diameters smaller than 15 nm without resorting to measurements at liquid helium temperature.

2. Experimental

2.1. Magnet construction

The magnet is shown in Fig. 1(a). Eight cuboidal permanent magnets (height = 19 mm, width = 19 mm, length = 120 mm, NdFeB, Ni-N52, ChenYang Technologies, China) are arranged in a Halbach array to produce a transverse magnetic field [38]. The

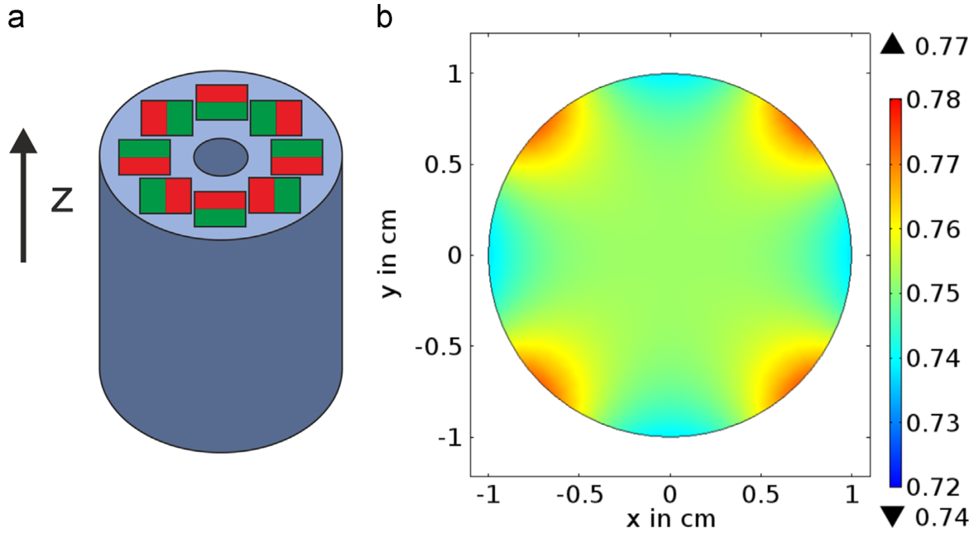

Fig. 1. Permanent magnets in a Halbach array for Mössbauer spectroscopy; (a) eight permanent magnets are arranged in a circle around an opening for the sample holder; (b) magnetic flux density norm distribution (Tesla) at the position of the sample holder inside the magnet as determined by finite element analysis using COMSOL. The minimum and the maximum value of the flux density within the region shown here are indicated with a triangle pointing upwards and downwards, respectively. The magnetic field points in the y-direction.