

Size effect of Mössbauer parameters in iron oxide nanoparticles

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Abstract The size dependence of Mössbauer parameters for iron oxide nanoparticles in the 10–25 nm range was investigated. It was shown that the isomer shift and hyperfine field parameters decrease with the nanoparticle size. Only at 25 nm the presence of magnetite was detected.

Keywords Mössbauer spectroscopy · Size effect · Iron oxide nanoparticles · Magnetite

1 Introduction

Magnetic iron oxide nanoparticles attract great attention of researchers since a long time because of their unusual physical properties. The most popular nanosized objects are magnetite Fe_3O_4 and maghemite $\gamma\text{-Fe}_2\text{O}_3$, because of their interesting magnetic properties, biocompatibility and biodegradability [1–3]. They can be used as contrast agents for NMR [4, 5], as well as key components for targeted drug delivery [4–6], hyperthermia [4, 7] and for magnetic isolation and separation of labeled cells [4, 8]. All these applications require a specific size distribution and their effectiveness strongly depends on the magnetic properties of used nanoparticles.

In contrast to bulk materials the characteristics of nanosize objects is strongly influenced by finite-size and surface effects and their contribution increases as the particle size decreases. It was shown that this property is responsible for a number of observed effects

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such as the appearance of a surface nonmagnetic layer [9], the temperature dependence of the magnetization changing with size [9, 10], the appearance of an oxidized surface layer [11] and the decrease of the hyperfine field with nanoparticle size [12].

Gamma-resonance (Mössbauer) spectroscopy is one of the most popular methods for studying nanoparticles containing iron. The Mössbauer spectrum depends strongly on nanoparticle size. Decreasing the nanoparticles size usually leads to a collapse of the hyperfine magnetic six-line structure to a quadrupole doublet or singlet. This occurs when the relaxation rate of nanoparticle magnetization vector becomes much faster than the Larmor frequency of the nuclear spin precession. In the opposite case of large nanoparticles, when the relaxation time is large enough to surpass the Larmor frequency, a well-resolved hyperfine magnetic structure with the Zeeman sextet of lines appears in the spectrum. The reverse process will occur when the measurement temperature rises. The Mössbauer spectrum of the superparamagnetic particles changes with increasing temperature from a Zeeman sextet to a paramagnetic doublet (or singlet).

2 Experiment

We used commercially available iron oxide nanoparticles (<http://www.oceannanotech.com/product.php?cid=69&pid=122>) with a carboxylic acid surface coating in form of a ferrofluid. The sizes of nanoparticles were previously determined by TEM and approximately equal to 10, 15, 20 and 25 nm, respectively. To prepare for the measurements the ferrofluid was dried to a powder state at 70 °C. Mössbauer spectra of nanoparticles were measured at 78 K and in applied external magnetic field of 30 kGs. The measurements were performed with a standard gamma-resonance spectrometer using a ^{57}Co (Rh) source. Mössbauer spectra were analyzed using the SPECTR program from the MStools package [13].

3 Results

For the Mössbauer spectra of 10–20 nm samples (Fig. 1) the simplest description consists of two sextets corresponding to iron in a tetrahedral (sublattice A) and octahedral (sublattice B) oxygen configuration. At 78 K, including extra temperature shift $\delta_T \sim 0.1$ mm/s relative to room temperature, the isomer shifts of the sextets should be approximately equal to 0.3–0.4 mm/s for sublattice A and 0.4–0.6 mm/s for sublattice B [14].

The sample of 25 nm demonstrates a different behavior. The preliminary analysis showed a significant increase in the shift of the center of gravity of the spectrum compared to the sample of 20 nm, which indicates the presence of ferrous iron. Furthermore, the external left line sextet is noticeably broader than right one, indicating the possible presence of magnetite (Fig. 2a).

The spectrum of the same sample at room temperature demonstrates a partial collapse to a broad doublet (Fig. 2b). This doublet is not typical for this size of nanoparticles, and its appearance can be explained by the features of the nanoparticles synthesis procedure. To the model of 2 sextets used above we should add an additional sextet, corresponding to ferrous iron.

For the unambiguous separation of these components, we used data derived from the analysis of this spectrum at room temperature (Fig. 2b). In this case, there are no difficulties to distinguish the components of ferrous iron because of differences in lineshapes. This

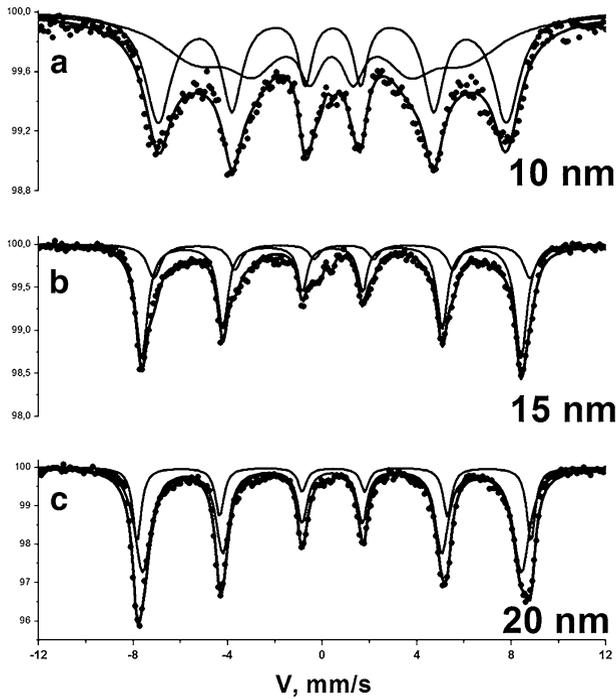


Fig. 1 Mössbauer spectra of 10–25 nm nanoparticles measured at 78 K

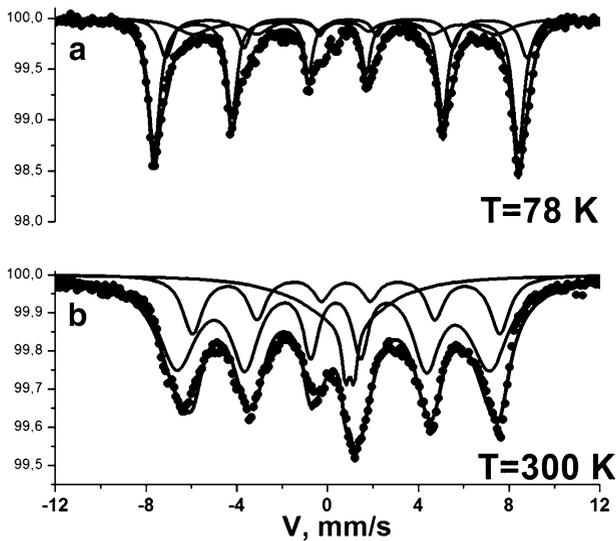


Fig. 2 Mössbauer spectra of 25 nm nanoparticles measured at 78 K and 300 K

circumstance allows us to use the ratio “A sublattice area/B sublattice area” as already found at 300 K for the analysis of the spectrum at 78 K. The results of the fitting procedure of the Mössbauer spectra at 78 K are shown in the Table 1.

Table 1 Mössbauer parameters of the spectra of nanoparticles 10–25 nm measured at 78 K: the center of gravity, isomer shifts and hyperfine field of each of the components

Size, nm	<IS>, mm/s	A sublattice		B sublattice	
		IS, mm/s	H _{hf} , kOe	IS, mm/s	H _{hf} , kOe
10	0.38(1)	0.36(2)	360(1)	0.43(2)	458(1)
15	0.44(1)	0.43(2)	493(1)	0.48(2)	512(1)
20	0.43(1)	0.43(2)	498(1)	0.49(2)	518(1)
25	0.50(1)	0.41(2)	499(1)	0.75(2)	414(1)

The dependence of the spectrum center of gravity shift on the nanoparticle size should be noted. In addition, the hyperfine field parameter of the spectrum of the 10 nm sample is much lower than that of other sizes. These facts point to the growing influence of surface to the characteristics of nanoparticles. Reducing the size of the nanoparticles increases the number of atoms in the oxidized surface layer [11], i.e. the concentration of ferric iron. On the Mössbauer spectrum it looks like a gradual reduction of isomer shift with decreasing size. Another effect that can be observed in samples of small enough particles is the increase in the anisotropy energy [12]. In this case, the Mössbauer spectrum demonstrates a decreasing hyperfine field as can be seen on sample of 10 nm (Fig. 1a). Thus, the dependence of the Mössbauer parameters of the surface area of nanoparticles exists. For 10–20 nm nanoparticles any noticeable presence of magnetite is not found, which can serve as confirmation of the existence of the critical radius for magnetite formation.

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