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Mössbauer studies of superparamagnetic ferrite nanoparticles for functional application

K. Mažeika · A. Jagminas · M. Kurtinaitienė

Abstract Nanoparticles of $CoFe_2O_4$ and $MnFe_2O_4$ prepared for functional applications in nanomedicine were studied using Mössbauer spectrometry. Superparamagnetic properties of nanoparticles of different size and composition were compared applying collective excitations and multilevel models for the description of the Mössbauer spectra.

Keywords Mössbauer effect · Nanoparticles · Functional applications · Ferrite

1 Introduction

Superparamagnetic nanoparticles of maghemite or magnetite have been studied for decades as the main constituent of ferrofluids. In recent years, moreover, many efforts have been made to apply magnetic nanoparticles in medicine. Applications for separation of cells, magnetic fluid hyperthermia and as carriers of drugs were previously considered [1–3]. Together with magnetite (maghemite), $CoFe_2O_4$ and $MnFe_2O_4$ nanoparticles were studied for biomedical applications. $MnFe_2O_4$ nanoparticles can be useful for biomedical diagnostics providing good properties as contrast agents [4]. Due to their higher magnetic anisotropy, $CoFe_2O_4$ nanoparticles may have advantage in hyperthermia applications [5, 6]. Mössbauer spectroscopy can be used not only to determine the composition of the nanoparticles, but also to experimentally study the superparamagnetic properties of nanoparticles. In this study we focus on the investigation of superparamagnetic nanoparticles of $CoFe_2O_4$ and

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$MnFe_2O_4$ prepared by co-precipitation using various growth stabilizers which are stable in water solution and suitable for biomedical applications.

2 Experimental

$CoFe_2O_4$ and $MnFe_2O_4$ nanoparticles were synthesized by co-precipitation at 70 °C and in autoclaves at 120–130 °C temperature using Co, Mn, Fe salts and NaOH at pH from 10.0 to 12.7. Citric acid was added as stabilizer. The composition and size of nanoparticles were determined by elemental analysis, XRD and Mössbauer spectroscopy, AFM and TEM (Fig. 1).

The Mössbauer transmission spectra (Fig. 2) were obtained from the nanoparticles dried onto a shred of filter paper using a Mössbauer spectrometer with a source of ^{57}Co(Rh) and a closed cycle helium cryostat. Hyperfine field distributions were used to determine the average hyperfine field $<B>$ (Fig. 2c). Moreover, models which take into account dynamics of the magnetic moment of the nanoparticles—the model of collective excitations and the multilevel relaxation model—were used. In the case of excitations of the magnetic moment at small angles the hyperfine field [7] can be expressed as

$$B \cong B_0 \left(1 - 0.5/\alpha\right), \tag{1}$$

where $\alpha = \Delta E \big/ k_B T$ is the relative barrier height, B_0 is the full hyperfine field, k_B is the Boltzmann constant and T is temperature. With a decrease in α a change of direction of the magnetic moment by 180° becomes more probable. The magnetic moment reversal or the Néel superparamagnetic relaxation time of non-interacting nanoparticles is given by

$$\tau = \tau_0 \exp\left(\alpha\right), \tag{2}$$

where τ_0 is the exponential prefactor.

The shape of partially collapsed Mössbauer spectra is better reproduced by the multilevel model [8].

A least square fitting procedure was used. When it was possible, two different subspectra, associated with tetragonal and octahedral sublattices with close but different hyperfine fields B_0, were used for a better fitting quality. Because $\alpha \propto V$, where V is the volume of a nanoparticle, the lognormal distribution of size of nanoparticles is taken into consideration by the lognormal distribution of α:

$$P\left(\alpha\right) = \frac{1}{\sqrt{2\pi}\sigma\alpha} \exp\left(-\frac{\ln^2\left(\alpha/\alpha_0\right)}{2\sigma^2}\right) \tag{3}$$

where α_0 is the median value of α and σ is the standard deviation. For simplicity of fitting the influence of interactions is not separated from the contribution of magnetic anisotropy and the energy of nanoparticle is approximated by

$$E\left(\theta\right) = \Delta E \sin^2\theta \tag{4}$$

where θ is the angle between the particle magnetic moment and the easy axis. In the case of the collective excitations model the sum $\sum_i P\left(\alpha_i\right) S\left(\delta, B_i\right)$ is used to fit the experimental spectra. The function S is a sextet having a hyperfine field B_{i} which is

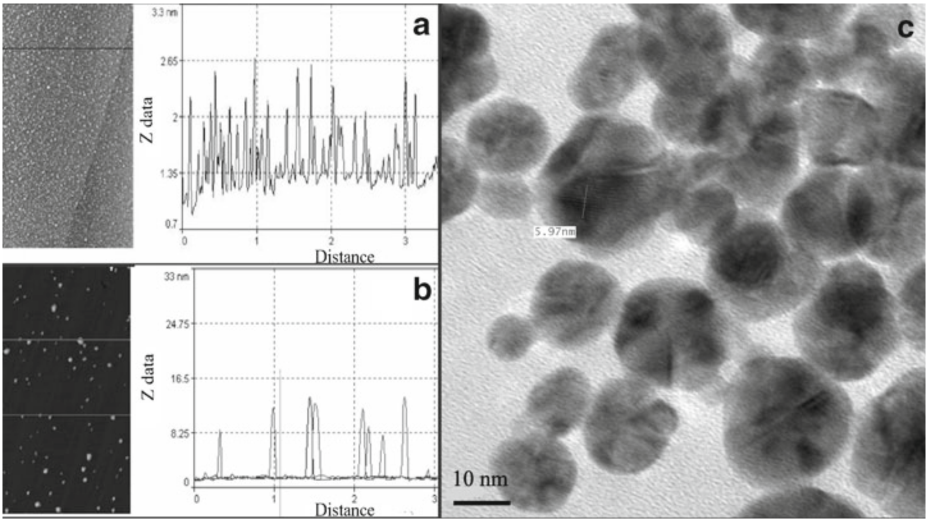

Fig. 1 AFM data for: **a** 2 nm, $CoFe_2O_4$, **b** 13 nm, $CoFe_2O_4$ and **c** TEM picture of 13 nm size $CoFe_2O_4$ nanoparticles

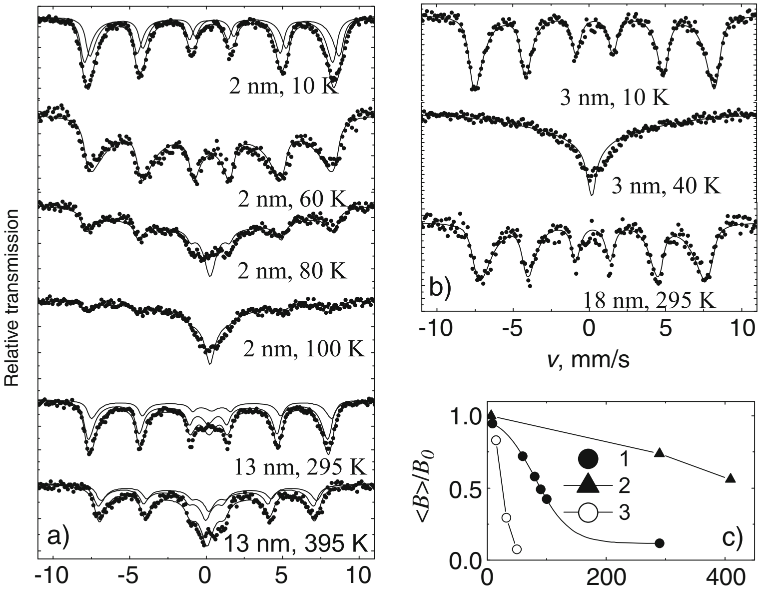

Fig. 2 Mössbauer spectra of: **a** $CoFe_2O_4$, **b** $MnFe_2O_4$ for indicated size and temperature and **c** dependence of the normalized hyperfine field. 1- $CoFe_2O_4$, 2 nm, 2- $CoFe_2O_4$, 13 nm 3 - $MnFe_2O_4$, 3 nm

evaluated using (1). The fitting parameters are the isomer shift δ, the median value α_0 and the standard deviation σ. The full hyperfine field B_0, the quadrupole shift and the line width are fixed to the values characteristic of bulk $CoFe_2O_4$ and $MnFe_2O_4$. When applying the multilevel model instead of one sextet the line shape is given by the expression $Re\left(\mathbf{WM}^{-1}\mathbf{1}\right)$ [8], where elements of the matrix **W** are probabilities of levels and the matrix **M** describes static positions and probabilities of jumps between the levels. The relaxation rate between levels, R, is an additional fitting parameter in the case of the multilevel model.

3 Results and discussion

The superparamagnetic transition temperatures when $B \approx 0.5\mathrm{B}_0$ are ≈30 K and ≈90 K for 3 nm size $\mathrm{MnFe_2O_4}$ and ≈2 nm size $\mathrm{CoFe_2O_4}$ nanoparticles, respectively, and are much higher than room temperature for 13 nm size $\mathrm{CoFe_2O_4}$ and 18 nm size $\mathrm{MnFe_2O_4}$ nanoparticles.

When the superparamagnetic transition temperature is below 90 K, the collective excitation model describes the spectra well even when the relative barrier height α decreases up to ≈2 (at ≈30 K temperature for $\mathrm{MnFe_2O_4}$ and ≈60 K for $\mathrm{CoFe_2O_4}$ nanoparticles, Table 1). The application of the multilevel model at these temperatures has shown that superparamagnetic relaxation time $\tau \approx 3\text{–}5{\cdot}10^{-8}$ s. The relaxation time τ is determined on the basis of the relaxation rate R and the relative barrier height α in the multilevel model [8, 9]. According to (2), τ depends on the exponential prefactor τ_0 and α. Both collective excitation and multilevel models are equivalent at slow diffusion limit when $\tau_0 = \sqrt{\pi}/\left(2R\alpha^{3/2}\right)$ is large [8, 9], but the multilevel model should be applied to reproduce the central superparamagnetic part of spectra for 13 nm $\mathrm{CoFe_2O_4}$ nanoparticles (Fig. 2a). The standard deviation is $\sigma =$ 0.2–0.6.

The ferrimagnetic nanoparticles are coated with a surfactant layer. Therefore dipolar interactions have to be considered to explain an increase in the prefactor τ_0. It is known that strong interactions can cause slowing down and freezing of spin dynamics [10, 11]. Moreover, the influence of dipole interactions, when applying the multilevel model, can be expressed by the introduction of the effective magnetic field H. This can be justified because the magnetic moments of nanoparticles arrange mostly in parallel when ordering of nanoparticles occurs in chains or in assemblies of interacting nanoparticles (dipolar ferromagnetism, superferromagnetism) [10, 11]. Then the effective magnetic field acts mostly along the easy magnetic axis of a nanoparticle. In the case of the collinear external magnetic field $H$the expression for the relaxation time of non-interacting particles (2) is modified to

$$\tau = \frac{\tau_0}{\left(1-h^2\right)(1+h)} \exp\left(\alpha\,(1+h)^2\right) \tag{5}$$

by introducing the ratio $h = mH/2KV$, where m is the magnetic moment of a nanoparticle, K is the magnetic anisotropy constant [8].

The value of the relative barrier height α determined by fitting depends on the energy dependence $E(\theta)$ applied in the models. Because $E(\theta)$ changes due to dipolar interactions the real value of the energy barrier for superparamagnetic relaxation can be larger (up to ≈2 times when $h \to 1$ in the case of the model of collective excitations). As the real value of α is larger, the real value of τ_0 is smaller in order to maintain the same superparamagnetic relaxation rate. Despite the fact that the contribution of dipolar interactions to the energy of a nanoparticle can be large, the description of experimental spectra by this simple models is sufficiently good.

Table 1 The Mössbauer spectra fitting parameters: median of the relative barrier height α_0, superparamagnetic relaxation time τ and exponential prefactor τ_0

Sample	T, K	α_0	τ_0,s	τ, s
$CoFe_2O_4$, 2 nm	9	16.4^a		
	60	2.1^a; 1.5^b	$6{\cdot}10^{-9}$	$3{\cdot}10^{-8}$
	80	0.9^a; 1.2^b	$1{\cdot}10^{-9}$	$5{\cdot}10^{-9}$
	100	1.1^b	$6{\cdot}10^{-10}$	$2{\cdot}10^{-9}$
$CoFe_2O_4$, 13 nm	295	7^b	$6{\cdot}10^{-11}$	$7{\cdot}10^{-8}$
	395	4.7^b	$6{\cdot}10^{-11}$	$7{\cdot}10^{-9}$
$MnFe_2O_4$, 3 nm	10	8.8^a		
	30	2.5^a; 0.8^b	$2{\cdot}10^{-8}$	$5{\cdot}10^{-8}$
	40	0.3^b	$6{\cdot}10^{-9}$	$9{\cdot}10^{-9}$
$MnFe_2O_4$, 18 nm	295	5^a		

[a] Collective excitation model
[b] Multilevel model

It is because only the energy levels having highest population probability (at energy minimum) are most important. The multilevel model is suitable for the evaluation of relaxation times near the blocking temperature. At higher temperature it describes the spectra less well. It does not describe all details in the center of the experimental spectrum because it does not consider the quadrupolar hyperfine interactions non-collinear to the magnetic hyperfine field. The better fits can be obtained by the multilevel model which uses Liouville superoperators as is shown in Ref. [9].

4 Conclusions

The superparamagnetic properties of nanoparticles prepared for functional applications in medicine were compared by applying Mössbauer spectroscopy data. The superparamagnetic transition temperature is higher and the superparamagnetic relaxation of nanoparticles having higher ($CoFe_2O_4$) magnetic anisotropy is slower at a similar nanoparticle size as compared with $MnFe_2O_4$ nanoparticles. The difference is not as large as expected, possibly due to deviation in the composition or the influence of magnetic interactions between closely packed nanoparticles.

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References

1. Hergt, R., Dutz, S., Müller, R., Zeisberger, M.: Magnetic particle hyperthermia: nanoparticle magnetism and materials development for cancer therapy. J. Phys. Condens. Matter **18**, S2919–S2934 (2006)
2. Liong, M., Lu, J., Kovochich, M., Xia, T., Ruehm, S.G., Nel, A.E., Tamanoi, F., Zink, J.I.: Multifunctional inorganic nanoparticles for imaging, targeting, and drug delivery. ACS Nano **2**(5), 889–896 (2008)
3. Wu, W., He, Q., Jiang, C.: Magnetic iron oxide nanoparticles: synthesis and surface functionalization strategies. Nanoscale Res. Lett. **3**, 397–415 (2008)
4. Shao, H., Yoon, T.-J., Liong, M., Weissleder, R., Lee, H.: Magnetic nanoparticles for biomedical NMR-based diagnostics. Beilstein J. Nanotechnol. **1**, 142–154 (2010)

5. Rosensweig, R.E.: Heating magnetic fluid with alternating magnetic field. J. Magn. Magn. Mater. **252**, 370–374 (2002)
6. Kim, D.-H., Nikles, D.E., Johnson, D.T., Brazel, C.S.: Heat generation of aqueously dispersed $CoFe_2O_4$ nanoparticles as heating agents for magnetically activated drug delivery and hyperthermia. J. Magn. Magn. Mater. **320**, 2390–2396 (2008)
7. Thomas, M.F., Johnson, C.E.: Mössbauer spectroscopy of magnetic solids. In: Dickson, D.P.E., Berry, F.J. (eds.) Mössbauer Spectroscopy, pp. 143–197. Cambridge University Press, Cambridge (1986)
8. Jones, D.H., Srivastava K.K.P.: Many-state relaxation model for the Mössbauer spectra of superparamagnets. Phys. Rev. B **34**, 7542–7548 (1986)
9. Chuev, M.A.: Multi-level relaxation model for describing the Mössbauer spectra of single-domain particles in the presence of quadrupolar hyperfine interaction. J. Phys. Condens. Matter **23**, 426003-1-11 (2011)
10. Morup, S., Hansen, M.F., Frandsen, C.: Magnetic interactions between nanoparticles. Beilstein J. Nanotechnol. **1**, 182–190 (2010)
11. Majetich, S.A., Sachan, M.: Magnetostatic interactions in magnetic nanoparticle assemblies: energy, time and length scales. J. Phys. D. Appl. Phys. **39**, R407–R422 (2006)