

Nuclear Magnetic Resonance in Hexaferrite/Maghemite Composite Nanoparticles

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Due to their bio-compatibility and non-toxicity, ferrimagnetic iron oxides are suitable for various medical applications. In the case of hyperthermia, the promising approach how to reach desired magnetic properties is to combine more phases into a composite material. A series of samples containing maghemite and M-hexaferrite was prepared by sol-gel method with subsequent thermal treatment where annealing temperature and time were varied. The samples were characterized by X-ray diffraction. In this paper we focused mainly on application of nuclear magnetic resonance spectroscopy to investigate these strongly inhomogeneous nanoparticle composites. Frequency-swept ⁵⁷Fe NMR spectra of nanoparticle samples were measured in a zero external magnetic field at 4.2 K. Utilizing differences in optimal excitation field strengths and in relaxation times, we were able to resolve NMR signal assigned to hexagonal ferrite of M-phase from signal which showed features attributed to maghemite.

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1. Introduction

Magnetic iron oxide particles of submicron and nanoscale dimensions are employed as functional materials in a variety of technical and biomedical applications. The composition of nowadays used biologically harmless ferrimagnetic oxide materials is based on maghemite (γ -Fe₂O₃) or magnetite (Fe₃O₄) spinel structure. Their synthesis is relatively simple; their magnetic properties however can be modified only by variation of the particle dimension or structural defects.

To improve the magnetic properties of particles for applications in magnetic fluid hyperthermia, attention is paid to more complex magnetic oxides. Optimization of chemical composition was searched for lanthanum manganese perovskites or Co-Zn spinel ferrites [1].

Another approach consists in applying of multiphase composite materials [1, 2], where the combined contribution of different magnetic phases makes it possible to appropriately adjust magnetization, coercivity, and remanence and consequently the shape of the hysteresis loop and heating effect due to the energy absorbed from ac magnetic field. In materials combining maghemite and hexaferrite, the pronounced difference in magnetic anisotropies enables to control magnetic properties of the composite mainly by the ratio of the two ferrimagnetic phases.

⁵⁷Fe nuclear magnetic resonance (NMR) spectroscopy proved to be successful in microstructure studies of magnetic iron oxides when the resonating ⁵⁷Fe nuclei serve as a local hyperfine field probe sensitive to atomic and magnetic arrangement in their vicinity [3, 4]. However, this experimental method has not been systematically applied to investigation of coexistence of two or more different magnetic phases with overlapping spectra.

This paper focuses on series of nanoparticle powder samples containing one or two ferrimagnetic phases, i.e. maghemite γ -Fe₂O₃ and strontium M-type hexaferrite SrFe₁₂O₁₉. The sample series was investigated by ⁵⁷Fe NMR.

2. Experimental

Series of nanoparticle samples with variable amount of maghemite and M-hexaferrite phases was prepared via sol-gel method with subsequent thermal treatment where annealing temperature and time were varied (Table). More details about preparation are given in [5, 6]. X-ray diffraction was applied to determine mean crystallite size d_{XRD} and phase composition. Besides maghemite and hexaferrite, hematite α -Fe₂O₃ and also SrCO₃ were detected.

NMR spectra were recorded at 4.2 K in zero external magnetic field using Bruker Avance pulse spectrometer. The sample was placed in the coil of a tunable parallel resonant circuit of in-house-made NMR probe. ⁵⁷Fe NMR frequency-swept spectra with typical frequency step of 50–100 kHz were acquired in a frequency range of 68–77 MHz using multipulse spin echo

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TABLE

Composite nanoparticle samples.

Sample	Annealing		Particle size d_{XRD} [nm]	Composition [%] (iron oxide phases)		
	Temp [°C]	Time [min]		Hexaferrite	Maghemite	Hematite
m1	550	180	9	0	98.6	0
m2	500	180	11	0	96.9	0
mh1	600	32	6	6.3	79.7	3.3
			(hex.)			
mh2	600	67	15	11.9	77.2	5.6
			(hex.)			
mh3	600	190	32	41.2	47.1	10.1
h1	700	22	32	78.0	0	22.0
h2	800	20	62	70.6	0	29.4
h3	800	146	81	75.1	0	24.9

Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence. Individual echoes formed in the sequence were summed and Fourier transformed.

In pulse NMR spectroscopy it is necessary to properly adjust amplitude of applied radiofrequency (rf) field pulses to reach optimal excitation of NMR signal. In the case of magnetic materials, the optimal rf field is strongly sample/phase-specific because it depends on rf field enhancement induced by hyperfine coupling of nuclear and electron spins [7]. The enhancement factor is expected to be significantly higher in maghemite than in magnetically hard hexaferrite $\text{SrFe}_{12}\text{O}_{19}$. Dependences of the NMR signal on rf field amplitude were therefore carefully measured for the studied samples. Delay time between pulse sequences and selection of summed spin echoes in CPMG train were other controlled parameters of acquisition and data processing.

3. Results and discussion

^{57}Fe NMR spectra measured in a range of 68–77 MHz are shown in Fig. 1. In the dependence of signal intensity on rf field amplitude obtained for samples m1 and m2 just one maximum appeared, delay time of tens of ms between scans was sufficient for full spin–lattice relaxation, also spin–spin relaxation was rather fast so that intensities of echo signals in CPMG train decreased considerably but homogeneously within the whole spectral range. Spectra of samples m1 and m2 (Fig. 1a) show typical shape corresponding to maghemite phase [8–12].

Also for samples h1, h2, and h3 the dependence of signal on rf field amplitude showed one maximum, this case at relatively stronger rf field, necessary delay time was about 1 s, spin–spin relaxation was significantly slower than for m1 and m2. Spectra of all three samples h1–h3 (Fig. 1b) correspond to M-hexaferrite structure [13, 14] and are very similar in line positions and widths. In comparison with single crystal of strontium M-hexaferrite, the spectral lines are substantially broadened and shifted from single crystal resonance frequencies (12k: 71.0420 MHz, $4f_{IV}$: 72.7210 MHz,

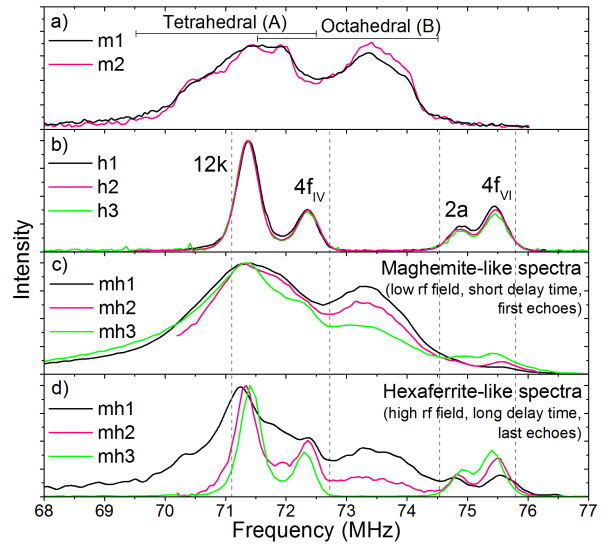


Fig. 1. ^{57}Fe NMR spectra of composite nanoparticle samples recorded in a zero external magnetic field at 4.2 K. Spectra are scaled to maximum of intensity. Assignment of spectral lines to tetrahedral A and octahedral B sites in maghemite and to 12k, $4f_{IV}$, 2a, $4f_{VI}$ sites in M-type hexaferrite is given. Dashed vertical lines show resonance frequencies in bulk strontium M-hexaferrite.

2a: 74.5390 MHz, $4f_{VI}$: 75.7940 MHz, [15]) by 0.31–0.33 MHz: lines of Fe^{3+} sites with “spin up” orientation (12k and 2a) are shifted to lower frequencies while the lines of “spin down” sites ($4f_{IV}$ and $4f_{VI}$) shift to higher frequencies. These shifts can be attributed mostly to contribution of demagnetizing fields and the shift values imply 0.22–0.24 T in magnetic field units (using ^{57}Fe gyromagnetic ratio 1.377 MHz/T) which corresponds to ellipsoidal particle shapes of a/c ratio about 0.98–0.89.

The remaining cases comprise composite samples mh1, mh2, and mh3. For each sample, a pair of spectra was recorded (Fig. 1c,d) to reflect the differences in optimal excitation and processing conditions of the two expected ferrimagnetic phases. Spectra in Fig. 1c are acquired using low rf field, short delay time and former echoes in the CPMG train while spectra in Fig. 1d are obtained with approximately five times stronger rf field, longer delay time and with processing of later echoes. Example of the dependences of signal intensity on rf field amplitude is given in Fig. 2 and shows also the differences due to delay times and processed echo numbers. Evidently, line-shapes in Fig. 1c bear a resemblance to maghemite spectra and the maghemite-like profile is more pronounced for shorter annealing time. Figure 1d shows that longer annealing results in hexaferrite-like spectral profile and a pure hexaferrite spectrum is seen for sample mh3 while the spectra of mh2 and mh3 are rather complex.

A more detailed analysis of the complex spectra of samples mh1 and mh2 in Fig. 1d (hexaferrite-like) and of samples mh1, mh2 and mh3 in Fig. 1c (maghemite-like) showed that they are not simple linear combinations of

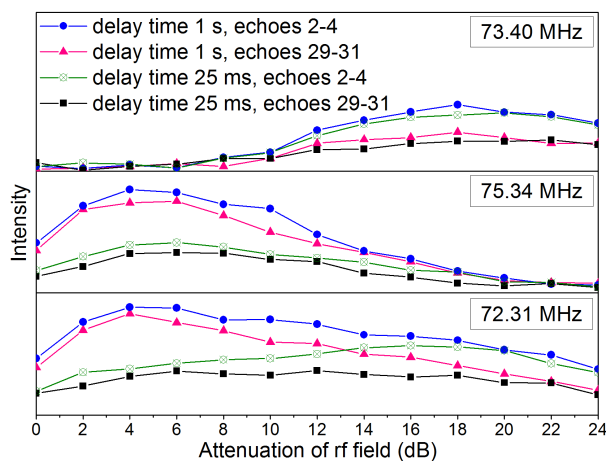


Fig. 2. Dependences of NMR signal intensity on the attenuation of applied rf field for pulse lengths in CPMG sequence $2/4 \mu\text{s}$, measured at frequencies 73.40 MHz (maghemite resonance), 75.34 MHz (hexaferrite) and 72.31 MHz (both phases).

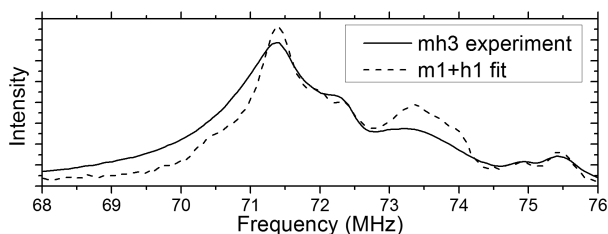


Fig. 3. Decomposition of NMR maghemite-like spectrum of sample mh3, based on linear combination of spectral profiles of maghemite and hexaferrite spectra of samples m1 and h1.

maghemite and hexaferrite spectral profiles. In Fig. 3 a decomposition of spectrum of sample mh3 is shown as an example. Spectral shapes observed in these cases may be brought about by an imperfect crystalline structure — structural defects, deviations from stoichiometry, stacking faults in hexaferrite or admixture of other hexaferrite building blocks/phases.

4. Conclusions

A series of nanocrystalline samples containing ferrimagnetic phases of maghemite and strontium M-type hexagonal ferrite was prepared by sol-gel technique. The ferrite content and particle size significantly increases with increasing annealing temperature, annealing time affects mostly particle size.

The sample series was investigated by ^{57}Fe NMR. ^{57}Fe NMR spectroscopy appeared to be useful in monitoring of maghemite and hexaferrite phases and in detection of coexistence of the two ferrimagnetic phases in composite samples. Proper choice of excitation and processing parameters allowed us (at least partially) to separate signals of maghemite and hexagonal ferrite.

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