

Structure of Iron Oxide Nanoparticles Studied by ^{57}Fe NMR

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In this work we apply nuclear magnetic resonance (NMR) spectroscopy of ^{57}Fe nuclei for investigation of submicron and nanocrystalline iron oxide systems. The studied iron oxide particles are obtained from ferrous hydroxide gels (prepared from FeCl_2 and KOH) by aging at elevated temperatures (90 °C) with KNO_3 as oxidant. The ^{57}Fe NMR spectra of the samples are measured in temperature range 4.2–370 K in a zero external magnetic field. Signals of ^{57}Fe nuclei assigned to tetrahedral and octahedral iron sites are well resolved. The NMR spectra and their temperature dependences are compared with those of stoichiometric and nonstoichiometric magnetite single crystals, as well as with samples of maghemite.

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1. Introduction

Nanoparticles and submicron-size particles of magnetic compounds are employed as functional materials in a variety of technical and medical applications. The characterization of their properties is usually performed with X-ray diffraction and standard macroscopic magnetic methods. In this work we focus on magnetite/maghemite system, which is complicated to fully handle with these methods because it is hard to distinguish magnetite from vacant magnetite or maghemite phase from X-ray diffraction pattern, whereas standard magnetic measurements are not able to provide much details on magnetic sublattices and their applicability for the mixed systems is limited. Therefore, our aim is to apply the ^{57}Fe nuclear magnetic resonance (NMR) method for studying these materials in order to take advantage of microscopic insight provided by this hyperfine method.

Above the Verwey transition temperature ($T_V \sim 120$ K), magnetite has a cubic inverse spinel structure, unit cell contains 8 tetrahedral (A) sites occupied by Fe^{3+} ions and 16 octahedral (B) sites with $\text{Fe}^{2.5+}$ ions – this can be expressed by the formula $[\text{Fe}_1]_A[\text{Fe}_2]_B\text{O}_4$. In between the Verwey transition and the spin reorientation transition (at ~ 130 K), the easy magnetization axis is [001], all A sites are magnetically equivalent as well as all B sites. Easy magnetization direction above spin reorientation transition is [111], all A sites are still magnetically equivalent, whereas 16 B sites are divided into 2 groups (B_1 , B_2) in 1:3 ratio. Below the Verwey transition, the structure of magnetite is monoclinic and the eight A and sixteen B sites are inequivalent. Each group of magnetically equivalent iron sites gives rise to one ^{57}Fe NMR signal line in spectra [1].

Maghemite structure (with cubic or tetragonal lattice)

can be understood as magnetite with vacancies (either randomly distributed or ordered) at octahedral sites, i.e. $[\text{Fe}_1]_A[\text{Fe}_{5/3}]_B\text{O}_4$. The ^{57}Fe NMR spectra of maghemite samples measured at room temperature and interpreted with a focus on tetrahedral and octahedral sublattice spectral components are reported in [2, 3].

2. Experiment

The investigated samples are obtained from ferrous hydroxide gels (prepared from FeCl_2 and KOH) by aging at elevated temperatures (90 °C), with KNO_3 as oxidant. The ^{57}Fe NMR experiments are carried out in a zero external magnetic field using spin echo CPMG pulse sequence on two samples of particle size distributions 30–60 nm and 80–110 nm. Spectra of both samples, measured at room temperature, are presented in Fig. 1 together with a spectrum of single crystal of stoichiometric magnetite [1]. Although spectral lines of the nanoparticle samples exhibit significant broadening compared to the single crystal magnetite, resonances of ^{57}Fe nuclei at A and B sites of magnetite can be easily resolved. As can be seen from comparison of spectrum of studied sample with particle sizes 80–110 nm, reference spectrum of polycrystalline maghemite [4] and spectrum of single crystal magnetite acquired at 4.2 K [1] (broadened by a convolution with Gaussian, provided in the Fig. 2), the spectrum of the investigated sample resembles some characteristics of maghemite spectrum. Temperature dependence of ^{57}Fe NMR spectra of nanoparticle sample (80–110 nm), covering temperature range from 4.2 to 370 K was also measured, see Fig. 3. As expected, temperature dependence of magnetization results in a frequency shift of the spectra. More importantly, significant variation of spectrum shape with temperature is observed.

3. Discussion

The comparison of spectra of nanocrystalline samples with stoichiometric single crystal magnetite at 298 K [1] (Fig. 1) reveals a match of resonance bands, whereas resonance lines in nanoparticle spectra are apparently broader due to a wide distribution of local magnetic fields

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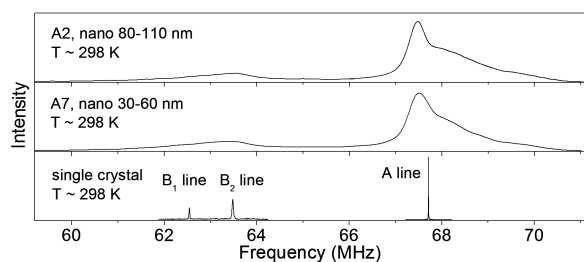


Fig. 1. The ^{57}Fe NMR spectra of nanoparticle samples and magnetite single crystal sample [1] acquired at room temperature.

at resonating nuclei, since the crystal and magnetic structure of nanoparticles is less perfect than in single crystals [5]. However, strong signal in the 66–71 MHz spectral region seems to contain maghemite A and B resonance lines [2-4, 6], beside magnetite A line. Close relation to maghemite is indicated also by the same resonance frequency range and similar spectral features in the spectrum of the studied sample at 4.2 K and in the maghemite spectrum [4] in Fig. 2.

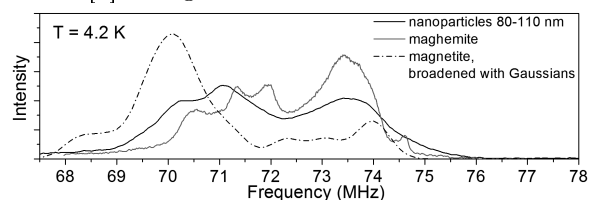


Fig. 2. Comparison of ^{57}Fe NMR spectra of nanoparticle sample (80–110 nm), maghemite [4] and stoichiometric single crystal magnetite [1] broadened by convolution with Gaussian, frequency range 68–78 MHz, 4.2 K.

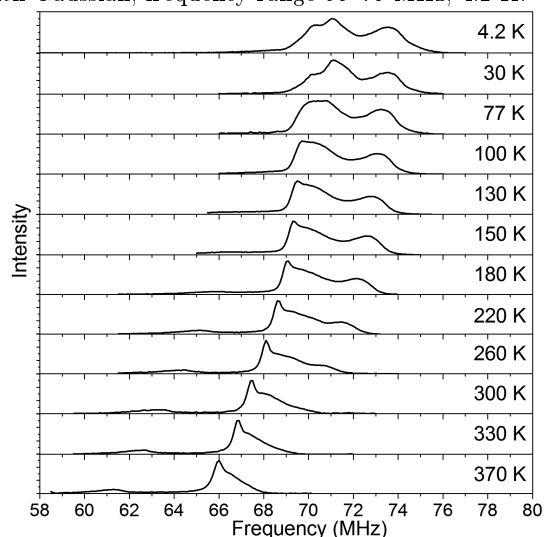


Fig. 3. The ^{57}Fe NMR spectra of nanoparticle sample (80–110 nm) measured at different temperatures.

In Fig. 4 frequencies of pronounced peaks in the spectra of nanoparticle sample are plotted as functions of temperature. The dependences closely match those of spectral lines of stoichiometric magnetite [1, 7] and main

lines and satellite lines S1, S2, and S3 in spectra of non-stoichiometric magnetite, where the satellite lines are induced by vacancies at octahedral (B) sites [8]. Moreover, a good correspondence with temperature dependences of ^{57}Fe NMR signals of maghemite [4] is also found.

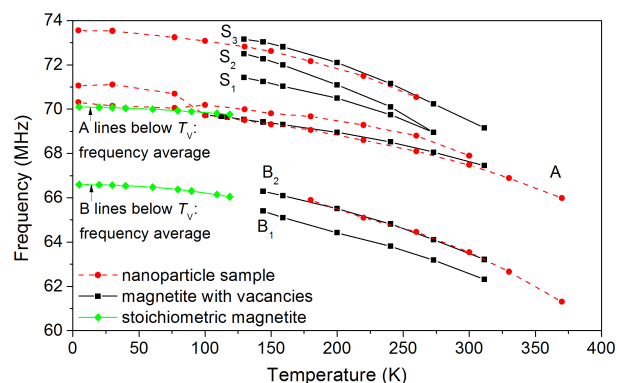


Fig. 4. Temperature dependence of ^{57}Fe NMR resonance frequencies. Nanoparticle sample (80–110 nm) compared to single crystals of stoichiometric magnetite [1, 6] and magnetite with vacancies $\text{Fe}_{3(1-\delta)}\text{O}_4$, $\delta = 0.009$ [7].

4. Conclusion

The ^{57}Fe NMR measurements on iron oxide particles, obtained from ferrous hydroxide gels by aging at elevated temperatures, is reported. The comparison of the NMR spectra of the studied samples with spectra of stoichiometric and nonstoichiometric magnetite single crystals and of polycrystalline maghemite, reveals qualitative agreement of spectral range and features thus identifying both magnetite and maghemite phases in the samples.

Acknowledgments

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