Magnetic Properties of Magnetite Formed by Biomineralization and Chemical Synthesis

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In this work, the magnetic properties of biologically produced magnetite (magnetosomes) by biomineralization process were compared to those of chemically synthesized Fe₃O₄. The coercivity of 185 Oe in magnetosomes is connected with the fact that the mean diameter is larger than critical size for transition from superparamagnetic to ferromagnetic behavior. A sharp magnetic transition at 105 K (Verwey transition) is clearly present in magnetosomes while in opposite, this transition is missing in Fe₃O₄.

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1. Introduction

Magnetic nanoparticles in diluted aqueous suspensions are an important tool in medical diagnostics as contrast agent for magnetic resonance imaging, in therapy for magnetic drug targeting or hyperthermia. For these applications there
were intensively used chemically synthesized magnetite nanoparticles. In recent years special nanoparticles the so-called magnetosomes were isolated, which consisted of a magnetic core covered by a protein-containing lipid membrane. Under controlled synthesis conditions, uniform particles of 20–45 nm core diameters may be produced which are of interest for a number of potential applications [1]. Magnetosome formation is achieved by a mineralization process with biological control over the accumulation of iron and the deposition of the mineral particle with specific size and orientation within a membrane vesicle at specific locations in the cell [2]. As sudden change in electric and magnetic properties of magnetite above 100 K has been a point of interest for many years, the aim of this paper is the comparison of magnetic and structural properties biologically produced and chemically synthesized magnetite nanoparticles.

2. Experimental

Bacterial magnetosomes investigated in this contribution are synthesized by magnetotactic bacteria *Magnetospirillum* sp. strain AMB-1. This bacterium is a Gram-negative α-proteobacterium that is more oxygen-tolerant and easier to grow on a large scale. Nowadays, the entire genome of *Magnetospirillum* sp. AMB-1 was sequenced annotated and analyzed [2]. Techniques for the isolation and purification of magnetosome particles from *Magnetospirillum* species are based on magnetic separation [3] or a combination of a sucrose-gradient centrifugation and a magnetic separation technique. These procedures leave the surrounding membrane intact and magnetosome preparations are apparently free of contaminating material. The chemically synthesized magnetite nanoparticles were prepared by co-precipitation method from ferric and ferrous salts in an alkali aqueous solution [4]. Magnetic properties of prepared aqueous suspensions were measured by SQUID magnetometer by Quantum Design in magnetic field (up to 5 T) and in temperature range 2–250 K. The morphological properties and size of magnetosomes and chemically synthesized nanoparticles were estimated from transmission electron microscopy (TEM) using JEOL1200EX Microscope working at 120 kV. The samples for TEM experiments were prepared on amorphous carbon foil by micropipetting of aqueous solution of magnetosomes and nanoparticles, respectively.

3. Results and discussion

In order to compare different samples we report temperature dependence of magnetization measurements. After samples were cooled in zero magnetic field to \( T = 2 \) K (zero field cooling, ZFC) magnetic field (500 Oe) was applied and magnetization was measured during the warming process. After reaching the temperature of 250 K (below melting point in our experiments) the system was cooled down without tuning off the magnetic field (field cooling, FC).
Fig. 1. ZFC and FC magnetization of various forms of magnetite in dependence on temperature at magnetic field 500 Oe and transmission electron micrographs (TEM).

Figure 1 shows ZFC and FC magnetization measurements for samples containing magnetite in various morphological forms, biologically synthesized magnetosomes and chemically synthesized nearly spherical nanoparticles, respectively. We can see that magnetite nanoparticles prepared chemically by the coprecipitation method are very well separated with mean diameter of about 10 nm. On the other side, magnetosomes in magnetotactic bacteria are arranged in chains with tendency to form bent chain in suspension so as to minimize their magnetic stray field energy. The reason for these phenomena is existence of lipid membrane surrounding magnetic core which prevents them to stick together by electrostatic repulsion [2, 5]. As was stated earlier elasticity may play a major role in the magnetosome arrangement into the bent configuration [6]. The mean size of magnetosomes estimated from TEM was 34 nm. It can be seen from ZFC and FC measurements that for the magnetosomes the Verwey transition (VT) is seen as sharp change in magnetic moment at transition temperature. This sharp change is missing in chemically synthesized magnetite and we can see the transition from blocked to superparamagnetic behavior in system with distribution of particle sizes only. The absence of the VT could be explained by reduction of barrier for magnetic moment reorientation in separated nanoparticles or as a consequence of lack of structural transition from cubic to triclinic symmetry for
smaller nanoparticles [7]. From the measurements the saturation magnetization of the magnetosomes was estimated to be 62 emu/g which is smaller than for chemically synthesized magnetite 75 emu/g at room temperature due to presence of nonmagnetic organic layer. The observed coercivity (185 Oe) at 293 K for magnetosomes can be connected with the fact that the mean diameter (34 nm) is larger than critical size for transition from superparamagnetic to ferromagnetic behavior [5]. On the other side, no coercivity was observed in chemically synthesized magnetite.

4. Conclusions

To conclude it can be said that a sharp magnetic transition (Verwey transition) at 105 K is clearly present in magnetosomes. The nanoparticles organized in chains act as long dipoles with enhanced magnetic anisotropy along the chains and thermal fluctuation are insufficient to overcome anisotropy barrier. In opposite, this transition is missing in Fe$_3$O$_4$ powder, where the magnetic nanoparticles are separated, the magnetic fluctuations are strong to overcome magnetic anisotropy and randomize magnetic moment.

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References