PIXE, PIGE and RBS Investigations of Ferrihydrite Nanoparticles Doped with Cobalt

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A big interest is paid to disperse magnetic nanoparticles based on iron nowadays [1]. Among iron oxyhydroxides, the greatest attention has been drawn to metastable ferrihydrite, the properties of which are determined by the composition, the structure, and the method used for the preparation of this compound [2]. The chemical formula of ferrihydrite is usually written in the following form: 5Fe2O3 · 9H2O. However, since ferrihydrite has a defect structure, the number of OH bonds can be changed. In ferrihydrite, there are two types of anion packings [3]. In the case of the formation of a ferrihydrite fragment with cubic packing, in which the anion planes are arranged in the sequence ABCABC, the Fe3+ ions are located in octahedral sites, thus forming two adjacent layers of octahedra occupied by iron atoms. At the same time, the formation of a ferrihydrite fragment with hexagonal packing, where the anion planes are arranged in the sequence ABAB (ACAC), leads to the formation of single layers of octahedra [4]. Ferrihydrite is formed in the core of a protein complex, namely, ferritin, which represents a protein cage of apoferritin (the outer and inner diameters are equal to 12 and 5–8 nm, respectively) [5]. This complex exists in organs of almost all higher animals and fulfills the function of iron storage (“depot”).

Massive ferrihydrite is an antiferromagnetic (AF) material. However, with a decrease in the size of antiferromagnetic particles to the nanometer scale, the magnetic properties of the material radically change. First, a decrease in the size of antiferromagnetic particles leads to an increase in the antiferromagnetic susceptibility, as well as to a change of its temperature dependence [6, 7]. Second, the field of the spin-flop transition becomes weaker and the Néel temperature of ferrihydrite particles decreases [8, 9]. Third (and this is a qualitatively new effect), the ferrihydrite nanoparticles acquire a constant magnetic moment, which is caused by the incomplete compensation of the magnetic moments of the sublattices in such small objects. As a result, from the magnetic point of view, each ferrihydrite nanoparticle is an unusual “hybrid” of the antiferromagnet and the ferrite. Owing to the unusual properties acquired during the transition to a nanodispersed state, the ferrihydrite particles can compete with nanoparticles of conventional ferromagnetic and ferrimagnetic materials used in various practical applications [10], including those for the targeted delivery of drugs in an organism, as well as for the contrast in magnetic resonance imaging [11].

Powders of undoped ferrihydrite nanoparticles and ferrihydrite nanoparticles doped with cobalt in the ratio of 5:1 have been prepared by hydrolysis of 3d-metal salts. It has been shown using Mössbauer spectroscopy, that cobalt is uniformly distributed over characteristic crystal-chemical positions of iron ions. The blocking temperatures of ferrihydrite nanoparticles have been determined. The nanoparticle sizes, magnetizations, surface anisotropy constants, and bulk anisotropy constants have been estimated. The doping of ferrihydrite nanoparticles with cobalt leads to a significant increase in the anisotropy constant of a nanoparticle and to the formation of surface rotational anisotropy with the surface anisotropy constant $K_u = 1.6 \times 10–3$ erg/cm^2.

Results on our previous experiment on biogenic ferrihydrite nanoparticles were presented at the International Balkan Workshop on Applied Physics 2017 and are submitted for publication in Romanian Reports on Physics journal.

For further and accurate investigations of the samples, we plan to apply methods of PIXE, PIGE, RBS, ERDA at 3 MV Tandetron in function at IFIN-HH Bucharest. We need 4 days for measurements.

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