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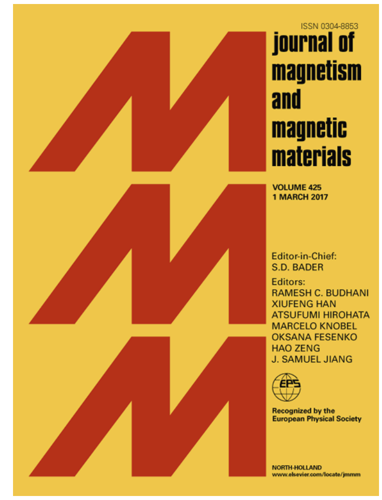

Structure and size dependence of the magnetic properties of Ni@C nanocomposites

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Structure and size dependence of the magnetic properties of Ni@C nanocomposites

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Abstract

Carbon-coated nickel (Ni) nanoparticles, Ni@C nanocomposites, have been synthesized using solid-state pyrolysis of nickel phthalocyanine and metal-free phthalocyanine $(NiPc)_x{\cdot}(H_2Pc)_{1-x}$ solid solutions, $0 \leq x \leq 1$. The Ni concentrations in carbon matrix (c_{Ni}) of the prepared samples continuously varied in the range of 0–3at.% (0–12wt.%). The average nanoparticle size varied within 4-40 nm range. All samples containing single domain Ni nanoparticles exhibit both ferromagnetic and superparamagnetic properties because of the wide range of size distribution. An abrupt drop of saturation magnetization has been observed with decrease in size of Ni nanoparticles from 40 nm to 12 nm. Nearly linear dependence of saturation magnetization on the nanoparticle surface/volume ratio can be interpreted as a result of contact interaction between Ni nanoparticles and the carbon matrix which provides an electron transfer from carbon matrix to nickel. However, further reductions in nanoparticle size increase magnetization growth of which can apparently contribute to the emergence of the giant paramagnetism due to large orbital moments of conductive electrons. The size effects and surface magnetic anisotropy in Ni@C nanocomposites are revealed in the measurements of coercive field, zero-field cooling (ZFC) susceptibility, blocking temperatures and ferromagnetic resonance spectra. Concentration dependencies of ferromagnetic and electron paramagnetic resonance parameters in Ni@C nanocomposites have also been investigated and their peculiarities highlighted. A correlation between concentration dependencies of FMR and SQUID magnetometry parameters, namely between the g-factor curves - g_{eff}, the resonance linewidth - ΔH_{FMR} and coercive field - H_c, have been observed.

Keywords: Ni@C nanocomposites, magnetic properties, size sffect, SQUID magnetometry, FMR, EPR, solid-phase pyrolysis, solidsulutions of phthalocyanines.

1. Introduction

In recent years, magnetic nanoparticles have become a topic of great interest from the scientific point of view, since their potential applications have become increasingly apparent. In particular, these nanomaterials are used in biomedicine, spintronics, catalysis, sensors, supercapacitors, etc [1–9]. Applications of magnetic metallic nanoparticles (M) encapsulated in a carbon (graphitic) shell (M@C), as carbon matrices exhibit high chemical and thermal stability. The carbon shell not only protects metal nanoparticles from oxidation, but also prevents their aggregation. In addition, carbon is a biocompatible material.

Currently, there are several methods for preparation of metal nanoparticles, including hydrothermal, arc discharge, laser ablation, chemical vapour deposition, pyrolysis, reduction of metal salts, solvothermal and aquollic methods, etc [1–3, 10–13].

We have developed highly facile, simple, safe and cost-effective one-step method which is based on solid-state pyrolysis of organic and metal-organic compounds. In Refs. [14–16] we presented a method of solid-state pyrolysis in metal phthalocyanines – MPc $[M(C_{32}N_8H_{16})$, M= Ni, Cu, Fe, Co, Zn] powders. Using this method, we obtained metallic nanoparticles in various carbon matrices. In this case, the atomic concentration of nickel metal is 3 at.%. We also discovered that solid-state pyrolysis of metal-free phthalocyanine – H_2Pc $[H_2(C_{32}N_8H_{16})]$ yields carbon microspheres, consisting of nanographite crystallites and amorphous carbon [17–19]. Diluting metal phthalocyanines with metal-free phthalocyanine and varying the solid-state pyrolysis parameters provides a unique opportunity to get insight into the dependences of structural and magnetic properties of nanoparticles on their size and concentration. One of the objectives of this work was preparation of metal phthalocyanine – metal-free phthalocyanine $(MPc)_x(H_2Pc)_{1-x}$, $0 \leq x \leq 1$ solid solutions. Pyrolysis of these solid solutions allows obtaining metallic nanoparticles in a range of concentration from 0 to 3 at.% (from 0 to 12 wt%).

In the present work we have syntesized nanocomposites in which the average size of Ni nanoparticles varies in a range from 4 nm to 40 nm. This was achieved by solid-phase pyrolysis of solid solutions $(NiPc)_x(H_2Pc)_{1-x}$, by changing composition - x and parameters of pyrolysis (temperature, time and pressure).

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