Small-angle neutron scattering investigations of Co-doped iron oxide nanoparticles. Preliminary results

Dorina Creanga, Maria Balasoiu, Dmitro Soloviov, Alexandra-Maria Balasoiu-Gaina, Emil Puscasu, Nicoleta Lupu, Cristina Stan

1 “Alexandru Ioan Cuza” University, Physics Faculty, Iasi, Romania
2 Joint Institute for Nuclear Research, Dubna, Russia
3 “Horia Hulubei” Institute of Physics and Nuclear Engineering, Bucharest, Romania
4 Moscow Technical Physics Institute, Dolgoprudny, Russia
5 Institute for Safety Problems of Nuclear Power Plants of the Ukrainian NAS, Kyiv, Ukraine
6 CMCF, Moscow State University, Moscow, Russian Federation
7 West University of Timisoara, Timisoara, Romania
8 National Institute of Research and Development for Technical Physics, Iasi, Romania
9 University “Politehnica” of Bucharest, Faculty of Applied Sciences, Physics Department, Romania

E-mail: balas@jinr.ru

Abstract. Preliminary small-angle neutron scattering investigations on aqueous suspensions of several cobalt doped ferrites (Co$_x$Fe$_{3-x}$O$_4$, $x=0; 0.5; 1$) nanoparticles prepared by chemical co-precipitation method, are reported. The measurements were accomplished at the YuMO instrument in function at the IBR-2 reactor. Results of intermediary data treatment are presented and discussed.

1. Introduction

Cobalt ferrite nanoparticles (CoFe$_2$O$_4$) represent promising materials for technological and medical applications [1-15]. Active works have been reported in connection with new developments in preparation methods [16-29] and properties investigation of resulted samples [30-36].

In the present paper preliminary small-angle neutron scattering investigations on aqueous suspensions of several cobalt doped ferrites (Co$_x$Fe$_{3-x}$O$_4$, $x=0; 0.5; 1$) nanoparticles prepared by chemical co-precipitation method, are reported.

The preparation of Co$_x$Fe$_{3-x}$O$_4$ with different Co doping levels ($x=0; 0.25; 0.5; 0.75; 1$) using the chemical co-precipitation method, was reported earlier [37] and the scanning electron microscopy analysis of the samples showed that the cobalt ferrite nanoparticles have spherical shapes and average sizes of 70 nm [37].

2. Experimental

Samples of Co$_x$Fe$_{3-x}$O$_4$ with different Co doping ratio ($x=0; 0.5; 1$) were prepared and preliminary small angle neutron scattering measurements performed.
2.1. Sample preparation
The investigated cobalt ferrite nanoparticles were prepared by a chemical route based on highly versatile and of low cost Massart’s method [38]. The iron compound source was the ferric chloride hydrated crystalline powders and the ferrous sulfate while the cobalt ions were provided by the cobalt sulfate. The high purity reagents were purchased from Sigma-Aldrich firm and used without additional purification.

Alkali synthesis medium was ensured based on hot 24% sodium hydroxide pouring under continuous stirring, while the stabilization of nanoparticles in aqueous suspension was accomplished with citric acid as capping agent (5 g citric acid in 10 ml deionized water for each about 4 g of ferrophase sample).

2.2. SANS experiment
Small angle neutron scattering (SANS) experiments were performed at the time-of-flight YuMO spectrometer [39] in function at the high flux pulse IBR-2 reactor, JINR Dubna. The Sonix+ software control system provides spectrometer operation [40]. The experiments were carried out at a sample-to-detector distances of 5.28 m and 13.04 m, resulting in a Q range of 0.007÷0.2 Å⁻¹. The sample diameter and thickness in the beam were 14 mm and respectively 1 mm. The measured neutron scattering spectra are corrected relative to the transmission and thickness of the sample, background scattering due to the experimental cuvette and the vanadium reference sample using the SAS software [41], providing a neutron scattering intensity in absolute units of cm⁻¹.

3. Results and discussion
In Figure 1 the experimental curves of small-angle neutron scattering from the aqueous solutions of three type of nanoparticles, i.e. Fe₃O₄, Co₀.₅Fe₂.₅O₄ and CoFe₂O₄, are given.

![Figure 1](image)

Figure 1. Small-angle neutron scattering experimental curves from aqueous solutions of nanoparticles: (a) Fe₃O₄ (red squares); (b) Co₀.₅Fe₂.₅O₄ (half-blue circles); (c) CoFe₂O₄ (green triangles).

The experimental data from the Q range of (0.007÷0.07) Å⁻¹ were preliminary fitted with the Programme FITTER [42] in the monodisperse approximation. Two axis ellipsoidal coreshell for Fe₃O₄ (a) and triaxial ellipsoidal coreshell for Co₀.₅Fe₂.₅O₄ (b) and CoFe₂O₄ (c) models, respectively, were obtained (Figure 2).
Figure 2. Model fit of experimental SANS curves in the Q range of (0.007÷0.07) Å$^{-1}$ using FITTER programme: (a) for Fe$_3$O$_4$ nanoparticles; (b) for Co$_{0.5}$Fe$_{2.5}$O$_4$; (c) for CoFe$_2$O$_4$.

The model parameters resulting from the data fitting are given in the Table 1.
Table 1. The results of the SANS experimental data model fitting in the Q range of (0.007÷0.07) Å⁻¹.

| Sample     | Model fit                  | Semiaxis of core [nm] | Thickness of shell [nm] |
|------------|----------------------------|------------------------|-------------------------|
| Fe₃O₄      | Two axis ellipsoidal coreshell | 21.1±0.1 ε=0.0054, eccentricity | 9.1±0.1 |
| Co₀.₅Fe₂.₅O₄ | Triaxial ellipsoidal coreshell | a=38.8±0.1 b=3.3±0.1 c=5.4±0.1 | 6.3±0.1 |
| CoFe₂O₄    | Triaxial ellipsoidal coreshell | a=21.2±0.1 b=6.1±0.1 c=9.9±0.1 | 10.5±0.1 |

4. Conclusions
Preliminary small-angle neutron scattering investigations on aqueous suspensions of several cobalt doped ferrites (CoₓFe₃₋ₓO₄, x=0; 0.5; 1) nanoparticles prepared by chemical co-precipitation method, were accomplished.

Small-angle neutron scattering measurements fitted in the Q range of (0.007÷0.07) Å⁻¹ showed for all the samples ellipsoidal coreshell model of 20÷40 nm. A difference between the scanning electron microscopy (SEM) and SANS results was determined. In the case of SEM, the particles could be aggregated and this fact can explain the obtained double value for the particle size, in comparison with those measured by SANS.

Further, the experimental data will be fitted in the next Q domain, (0.07÷0.02) Å⁻¹ and the polydispersity will be considered.

Acknowledgements. JINR-RO Projects 219/10.04.2017 and 220/10.04.2017 item 62 and JINR-RO Projects for 2018 year are acknowledged.

References
[1] Shenker H 1957 Phys.Rev. 107 1246
[2] Jordan A, Wust P, Fahling H, John W, Hinz A and Felix R 1993 Int. J. Hyperthermia 9 51
[3] Kitamoto Y, Kantake S, Shirasaki S, Abe F, Naoe M 1999 J. Appl. Phys. 85 4708
[4] Ngo A-T and Pileni M-P 2000 Adv. Mater. 12(4) 276
[5] Fortin J P, Wilhelm C, Servais J, Menager C, Bacri J C, Gazeau F 2007 J. Am. Chem. Soc. 129 2628
[6] Kim D H, Nikles D E, Johnson D T, Brazel C S 2008 J. Magn. Magn. Mater. 320 2390
[7] Creangă D E, Iacob Gh, Ursache M, Nădejde C, Răucuciu M 2008 J Optoelectron Adv Mater. 10(3) 628
[8] Zi Z, Sun Y, Zhu X, Yang Z, Dai J, Song W 2009 J. Magn. Magn. Mater. 321 1251
[9] Gao J, Gu H, Xu B 2009 Acc. Chem. Res. 42(8) 1097
[10] Kami D, Takeda S, Itakura Y, Gojo S, Watanabe M, Toyoda M 2011 Int. J. Mol. Sci. 12 3705
[39] Kuklin A I, Islamov A K, Gordeliy V I 2005 Neutron News 16(3) 16
[40] Kirilov A S, Litvinenko E I, Astakhova N V, Murashkevich S M, Petukhova T B, Yudin V E, Gordelii V I, Islamov A Kh, Kuklin A I 2004 Instruments and Experimental Techniques 47(3) 3
[41] Soloviev A G, Solovieva T M, Stadnik A V, Islamov A Kh, Kuklin A I 2003 SAS The Package for Small Angle Neutron Scattering Data treatment. Version 2.4. Long write-Up and User’s Guide (Russian) JINR Communication P10-2003 86; http://wwwinfo.jinr.ru/programs/jinrlib/sas/indexe.html
[42] Soloviev A G, Stadnik A V, Islamov A H and A.I.Kuklin A I 2008 Fitter. The package for fitting a chosen theoretical multi-parameter function through a set of data points. Application to experimental data of the YuMO spectrometer. Version 2.1.0. Long Write-Up and User's Guide. Communication of JINR E10-2008-2; http://wwwinfo.jinr.ru/programs/jinrlib/fitter/docs/html/node2.html