Spectroscopic properties of superparamagnetic $\text{Fe}_m\text{O}_n$-$\text{SiO}_2$ 
nanoparticle colloidal solutions

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Abstract. The investigation of optical and electron spin resonance (ESR) spectroscopic properties are carried out. Six characteristic absorption bands related to distinctive conglomerates of $\text{Fe}_m\text{O}_n$ formed via sol-gel synthesis process on $\text{SiO}_2$ porous matrix are observed in optical spectra. ESR spectra investigation makes it possible to reveal small characteristic signal associated with magnetostatic interactions between conglomerates of $\text{Fe}_m\text{O}_n$ nanoparticles.

1. Introduction
The development of novel medical diagnostics methods such as magnetic resonance imaging (MRI), positron emission tomography, X-ray computed tomography has required further research in the field of agents for contrast-enhanced imaging [1]. Composite superparamagnetic $\text{Fe}_m\text{O}_n$ nanoparticles may be considered as negative contrast agents reducing spin-spin relaxation time. The possibility of synthesis of 10 nm $\text{Fe}_m\text{O}_n$-$\text{SiO}_2$ composite nanoparticles sustaining magnetic hysteresis properties is of great interest. Furthermore, due to their biocompatibility magnetic nanoparticles may be also used as magnetic drug-targeting agents [2] and as a potential medium for magnetic hyperthermia in high-frequency alternating magnetic field [3]. Optical properties of thin magnetite films are of great importance: such films demonstrate UV absorption and decent transmission in visible region allowing to consider nano-sized magnetite as a promising optoelectronic material [4]. Superparamagnetic nanoparticles $\text{Fe}_m\text{O}_n$ could be used in a wide variety of circumstances due to conjunction of important characteristics with peculiarities of chemical composition and magnetic properties.

2. Experimental methods
Colloidal composites $\text{Fe}_m\text{O}_n$-$\text{SiO}_2$ were formed via two stage sol-gel synthesis process. The first stage consisted in tetraethoxysylane (TEOS) sol synthesizing. Aqueous solution of ammonia was used to precipitate the gel. After 72 hours of gel desiccation at room temperature thermal treatment of $\text{SiO}_2$ powders at 300 °C was carried out.

At the second stage emulsification of highly dispersed $\text{SiO}_2$ was conducted by using ultrasonication treatment in aqueous solution of $\text{Fe}^{3+}$ and $\text{Fe}^{3+}$ chlorides. Then, $\text{Fe}_m\text{O}_n$ nanoparticles were deposited according to the following reaction:
FeSO₄ + 2FeCl₃ + 8NH₃•H₂O → Fe₃O₄↓ + 6NH₄Cl + (NH₄)₂SO₄ + 4H₂O

The sediment was dried at room temperature after being formed in the solution. In order to analyze chemical composition and magnetic properties of colloidal nanoparticles the sediment was investigated by ESR method. The investigation presented in this thesis had two distinct objectives. The first objective was to identify parameters of the optical absorption spectra of colloidal solutions of magnetic nanoparticles and to create the structure model of a single composite FemOn-SiO₂ nanoparticle. Specord® 40 Analytik Jena was used to fulfill optical absorption spectra measurements of the samples at the temperature of 300K. ESR spectra were obtained by using ESR-spectrometer JEOL at room temperature. Fe₃O₄ powder was irradiated with Co⁶⁰ β-ray source to dose 10⁶ rad.

3. Experimental results

According to P. Levy [5], the shape of the absorption bands is considered to be Gaussian as in equation (1);

\[ E(\nu) = K_0 \exp \left[ -\frac{4\ln2}{U^2}(\nu - \nu_0)^2 \right], \]  

where \( K_0 \) corresponds to absorbance at the wavelength of an absorption band maximum, \( U \) is the half-width of an absorption band (cm⁻¹) and \( \nu_0 \) is the position of an absorption band maximum (cm⁻¹). The appearance of absorption spectra (figure 1) of colloidal solutions indicates the identity of the chemical composition.

![Figure 1. The absorption spectra of colloidal solutions of superparamagnetic nanoparticles Fe₃O₄-SiO₂ in the visible and near UV range; the parameter is the concentration of TEOS during synthesis.](image)

Alternation in the concentration of Fe₃O₄ nanoparticles deposited on the SiO₂ gel matrix during the Massart reaction is obvious and the largest concentration of Fe₃O₄ nanoparticles is detected while using a solution of TEOS in isopropanol with the concentration of TEOS 60 vol. %.

The result of mathematical simulation of absorption spectra using Origin© 8.1 for colloidal solution with 60 vol. % TEOS concentration is shown on figure 2.
The approximation result of absorption spectrum via Gaussian curves (60 vol. % TEOS concentration): 1 – initial absorption spectrum, 2-7 – absorption bands corresponding to 25130 cm⁻¹, 26220 cm⁻¹, 27300 cm⁻¹, 28480 cm⁻¹, 29530 cm⁻¹ and 30480 cm⁻¹, 8 – absorption spectrum approximation.

As one can see in the figure 2 six distinctive absorption bands in UV region corresponding to the following maxima are found: 25130 cm⁻¹, 26220 cm⁻¹, 27300 cm⁻¹, 28480 cm⁻¹, 29530 cm⁻¹ and 30480 cm⁻¹ with intrinsic half-width remaining constant. The presence of these bands is attributed to Fe₃O₄ conglomerates with six characteristic dimensions on the surface of the gel matrix. Absorption maxima observed at a concentration of TEOS 60 vol. % and associated with conglomerates of all sizes are caused by the interaction of clusters (figure 3). Cluster size is estimated using G. Mie Theory [6].

According to equation (2),

\[
K_{\max} \Gamma = A \pi R^3 / 3,
\]

where \(K_{\theta}\) corresponds to absorbance at the wavelength of an absorption band maximum, \(\Gamma\) – is the half-width of an absorption band (cm⁻¹), \(A=1.25 \times 10^2\) eV/mm is the optical constant, \(R\) – colloidal particles radius, \(n\) – concentration of the nanoparticles (cm⁻³). Calculated radii of clusters turn out to be \(R = 1.9\) nm, 1.8 nm, 2.07 nm, 1.5 nm, 2.57 nm, 3.02 nm with respect to 25130 cm⁻¹; 26220 cm⁻¹; 27300 cm⁻¹; 28480 cm⁻¹; 29530 cm⁻¹; 30480 cm⁻¹ absorption bands (at 60 vol.% TEOS concentration).

The dependence of the maximum optical density \(D_{\text{max}}\) upon the concentration of TEOS for six characteristic absorption bands.
One can see in figure 4 ESR spectra of initial (signal 1) and γ-irradiated (signal 2) samples of sedimanted Fe₃O₄-SiO₂ powders. Initial Fe₃O₄ sample reveals slightly asymmetric line in the range of B = 3450 G (g=2.04). Similar signal was obtained in paper [7] dedicated to investigation of temperature and frequency dependences of Fe₃O₄ nanoparticle magnetic properties. According to [8] the aforementioned wide (ΔB ≈ 680 G) line resulted from relaxation in finite-sized nanoparticles. It is worth mentioning that similar line was observed [9] in ESR spectrum of x Fe₃O₄ – (100 - x) SiO₂ amorphous system (x = 0,1…9,5) synthesized via sol-gel technology.

Taking in consideration ESR spectrum of γ-irradiated sample one can see a signal of low intensity located on low energy side of general signal (g=2.04) at the value of g=2.08. Ionizing radiation impact seems to be followed by emergence of radiation defects in silicate matrix. [10]

![Figure 4. ESR spectra of initial and irradiated Fe₃O₄-SiO₂ powder samples.](image)

### 4. Conclusions

Composite magnetic nanoparticles Fe₃O₄-SiO₂ are investigated by using optical absorption spectroscopy method with respect to G. Mie theory. The presence of six distinctive absorption bands associated with the formation of Fe₃O₄ conglomerates on the surface of the gel matrix is revealed. Approximate estimation of conglomerate dimension correlates with results acquired in [11].

In ESR spectra of both non-irradiated and irradiated samples slightly asymmetric line at the value of g=2.04 is found. The existence of this band may be related to radiochemical reactions followed by transformation of Fe³⁺ to Fe⁵⁺. The signal at the value of g=2.8 is associated with magnetostatic interactions between conglomerates of Fe₃O₄ nanoparticles.

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