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SPECTRAL DEPENDENCIES OF MAGNETOOPTICAL EFFECTS IN MAGNETIC FLUIDS

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The spectral dependences of the transmittance and optical anisotropy effects in magnetic fluid have been investigated. It is shown that the refractive index spectra of bulk magnetite known are of little use for the quantitative and qualitative interpretation of optical effects in magnetic fluids. The transmission, birefringence, and dichroism spectra are calculated using the known refractive index spectra of magnetite. The best agreement with the experiment was obtained using the experimental spectra of the complex refractive index of the powder of magnetite nanoparticles. It is concluded that there is a significant difference in the spectra of the complex refractive index for bulk and nanosized magnetite.

Keywords: magnetic fluids, optical anisotropy, magnetite, complex refractive index.

Introduction

Magnetic fluids (ferrofluids, magnetic nanofluids) are colloids of nanoparticles of ferro- and ferrimagnets in various liquid media. To prevent coagulation under the action of van der Waals and magnetic dipole-dipole interactions, the surface of the particles is coated with molecules of a surfactant. Due to stabilization, magnetic fluids remain stable for a long time. Such media are unique systems in which the interaction of particles with an external magnetic field leads to interesting physical effects [1-2]. They were first developed in the early 1960s at NASA to control the flow of propellant under weightless conditions [3]. Subsequently, magnetic fluids have received a wide range of applications, such as: magnetic fluid dampers, bearings and seals [4], micromechanical systems [5], non-destructive testing devices [6], microfluidics devices [7], biosensors for studying cellular toxicity, and systems for treating oncological diseases by the method of hyperthermia [11], etc. Magnetic fluids under the influence of a magnetic field exhibit some different optical effects, such as birefringence [12-13], linear and circular dichroism [14], Faraday rotation and ellipticity [15], changes in the intensity of transmitted, scattered and reflected light [16-17], etc. Due to these effects, magnetic fluids are used in various magneto-optical devices: optical filters, limiters and gates, waveguides and fiber-optic modulators, diffraction gratings with a controlled period, optical sensors of magnetic field, static and dynamic displays, etc. [18]. When studying magneto-optical effects in magnetic colloids, monochromatic radiation sources, lasers, are usually used. When studying the spectral dependences of optical effects in magnetic fluids, transmission spectra are mainly studied [19]. The spectra of the effects of magnetic birefringence and dichroism were studied in [13, 20]. For the theoretical interpretation of optical effects in magnetic colloids and predicting the properties of magneto-optical devices, accurate data on the optical properties of colloidal particles and a dispersion medium are required. Such information can be obtained based on data from studies of the spectra of optical effects.

In this work, we present the results of experimental studies of the spectral dependences of optical effects in kerosene based magnetic fluids in the visible region. Earlier, in [18], we determined the spectra of the complex refractive index of magnetic colloids with different concentrations of the solid phase. This work aims to interpret the spectral dependences of optical effects in magnetic colloids using our data and those known from the literature on the spectra of the complex refractive index of magnetite.

1 Experimental technique

To study optical effects in magnetic fluids, a setup based on the Ellips-1891 spectral ellipsometer was used. We measured the ellipsometric parameters in transmitted light, as well as the transmission spectra of samples in the wavelength range of 350-1050 nm, in 5 samples of magnetic fluid with volume concentrations from 0.01% to 1%. All samples were obtained by dilution from the original magnetic fluid with a concentration of about 10%. For research, the samples were placed in rectangular glass cuvettes with a thickness of 1 to 5 mm. We investigated the following optical parameters of the samples: transmittance (the ratio of the intensities of the incident and transmitted light $T=I/I_0$) and, at the same time, optical density (D), change in optical density under the action of a field $(D_H-D_0)/D_0$, as well as ellipsometric parameters Ψ and Δ, determining the state of the polarization ellipse of the transmitted or reflected light. Using Δ, the main parameter of birefringence was calculated - the difference between the refractive indices of the extraordinary and ordinary rays $\Delta n = n_{\parallel} - n_{\perp}$, and according to Ψ data - the dichroism parameter $\Delta k = k_{\parallel} - k_{\perp}$. Helmholtz coils mounted on a sample stage in an ellipsometer were used to create a magnetic field.

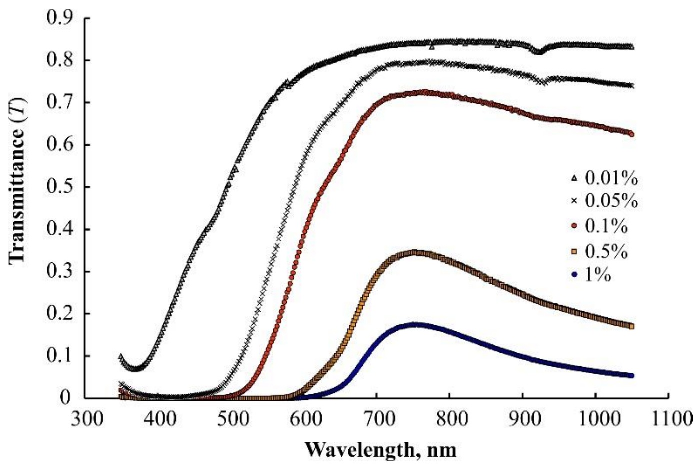

Fig. 1. Transmission spectra of magnetic fluids with different concentrations in a 1 mm thick cuvette.

Also, by the method of ellipsometry in reflected light, a sample of a powder of magnetite nanoparticles 10 nm in size, pressed into a tablet with a diameter of about 13 mm under a pressure of 100 MPa, were investigated. The density of the compressed nanoparticle powder was 2360 kg/m^3, which corresponds to a volume concentration of about 37%. The nanoparticle powder was obtained by prolonged drying of a magnetic fluid based on kerosene, which suggests the presence of a certain amount of oleic acid in it. In Fig. 1 shows the transmission spectra of samples of magnetic fluids with different concentrations of the solid phase. A characteristic feature of the spectra is the presence of a transmission maximum in the 720–750 nm region, which becomes more pronounced with an increase in the particle concentration.

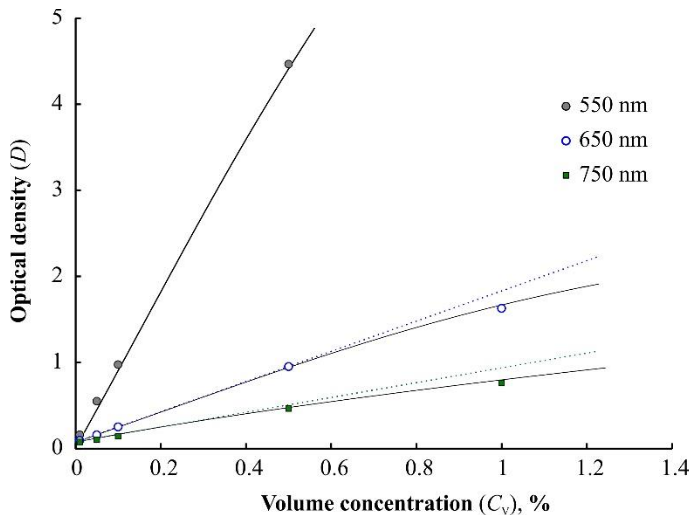

Fig 2. Dependences of the optical density of various samples of a magnetic fluid on the volume concentration of the solid phase

In Fig. 2 shows the dependences of optical density on concentration at three different wavelengths. We found that the effect of the magnetic field on the light transmission of the samples is rather weak. For samples with a concentration of less than 0.5%, within the experimental error, no changes in transparency were observed upon exposure to a field. The relative change in optical density under the action of the field did not exceed a few percent (Fig. 3). In Fig. 4 and Fig. 5 show the spectra of the effects of birefringence and dichroism in a magnetic fluid with a concentration of 0.01%.

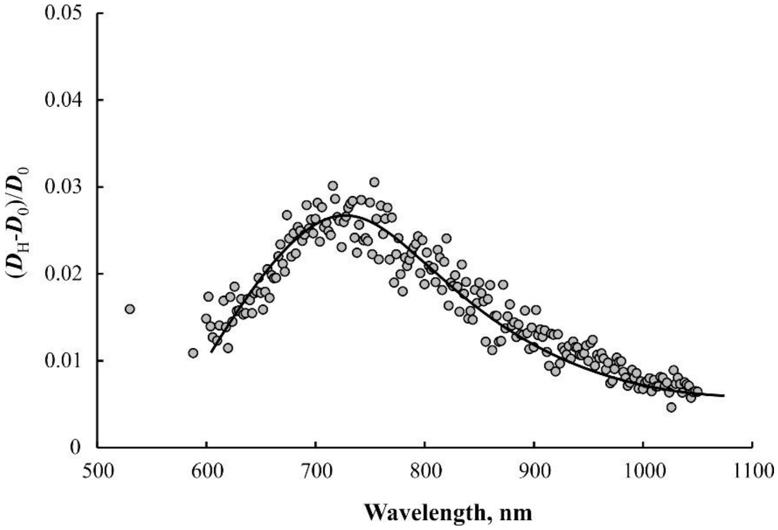

Fig. 3. Spectral dependence of the relative change in the optical density of a sample with a concentration of 1% under the influence of a constant magnetic field *H*=200 Oe

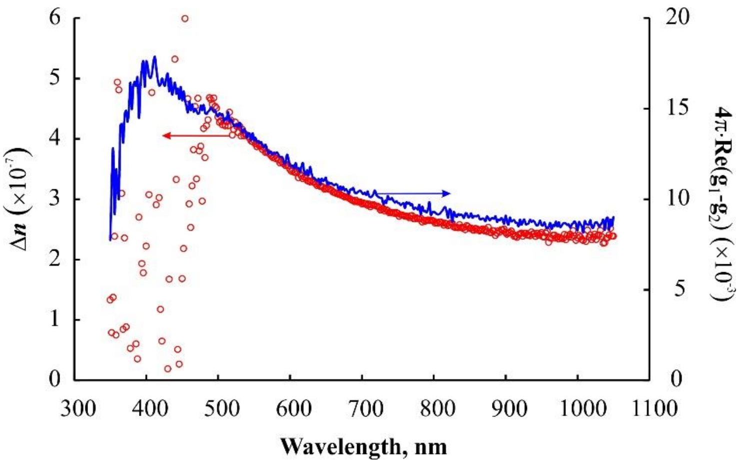

Fig. 4. Birefringence spectrum in a sample with a concentration of 0.01% when exposed to a magnetic field *H*=50 Oe and calculation of the real part of optical anisotropy

2 Results and Discussion

The interpretation of the spectral dependences of the transmittance of magnetic colloids with a not too high concentration of particles can be constructed on the basis of the Bouguer-Lambert law [19], according to which:

$$T = \frac{I}{I_0} = \exp(-\sigma_{ext} NL). \tag{1}$$

here σ_{ext} is the cross -section of light attenuation by an individual particle, N is the number concentration of particles, *L* is the light path length. From (1) it follows that the optical density of the medium should be proportional to the concentration of particles:

$$D = \lg\left(\frac{I_0}{I}\right) = 0.43\sigma_{ext} NL\,. \qquad (2)$$

The validity of expression (2) for samples with a low concentration is confirmed by Fig. 2, from which it can be seen that a direct proportionality between the concentration of particles and optical density takes place up to a concentration of about 0.3-0.4%, and the linear dependence remains for different wavelengths, albeit with a different slope. With increasing concentration, increasing deviations from the linear dependence are observed, which can be explained by the effects of multiple scattering of light in dense media. When exposed to an external field, the colloid acquires optical anisotropy. The simplest anisotropy mechanism is the orientational ordering of the long axes of nonspherical particles along the direction of the external field [10]. More complex mechanisms of optical anisotropy in a magnetic colloid are associated with the formation of ordered structures under the action of a field: chains, labyrinths, or quasicrystalline formations of nanoparticles similar to a photonic crystal [15]. The uniaxial optical anisotropy induced by an external field can be described by the diagonal refractive index tensor. This leads to the appearance of birefringence in the colloid and a change in the light extinction. The refractive and extinction indices of light become different for light polarized along and across the applied field $n_{\|} \neq n_{\perp}$ and $k_{\|} \neq k_{\perp}$, where indices || и ⊥ denote the orientation of the polarization of light with respect to the direction of the optical axis, i.e. direction of the external field.

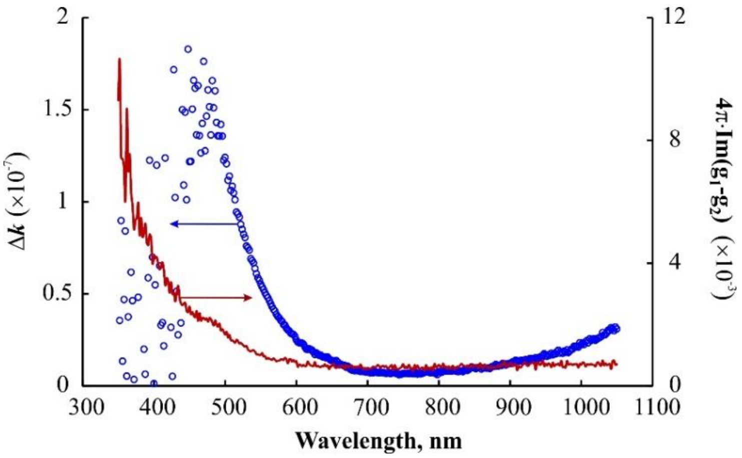

Fig. 5. Dichroism spectrum in a sample with a concentration of 0.01% when exposed to a constant magnetic field H=50 Oe and calculation of the imaginary part of optical anisotropy.

Following [10, 20], birefringence and dichroism in a colloid of single-domain magnetic particles under the action of an external magnetic field can be described by the expressions:

$$\Delta n = \frac{2\pi C_V}{n_k}\mathrm{Re}(g_1 - g_2)\cdot\Phi(\xi,\sigma), \qquad \Delta k = \frac{2\pi C_V}{n_k}\mathrm{Im}(g_1 - g_2)\cdot\Phi(\xi,\sigma), \qquad (3)$$

where C_V is the volume concentration of particles, $g_1 - g_2$ is the optical anisotropy of the particle, $\Phi(\xi,\sigma)$ is the orientation function determined by the ratio of the energy of the particle in the magnetic field and the energy of anisotropy to the thermal energy: $\xi = mH/kT$ and $\sigma = KV/kT$. In expression (3), only the optical anisotropy is dependent on the wavelength of light, the formula for the components of which has the form:

$$g_{1,2} = \frac{n_k^2}{4\pi}\cdot\frac{\tilde{n}_m^2 - n_k^2}{n_k^2 + N_{1,2}(\tilde{n}_m^2 - n_k^2)}, \qquad (4)$$

where $N_{1,2}$ are demagnetizing factors along the short and long axes of the particle, respectively, n_k is the refractive index of the dispersion medium (kerosene). Fig. 4 and 5 shows the dependencies $\mathrm{Re}(g_1 - g_2)$ and

$\mathrm{Im}(g_1 - g_2)$ as a functions of the wavelength calculated for the spectrum of the complex refractive index of the powder of magnetite nanoparticles. It can be seen that the shape of the dependence is in very good agreement with the results of birefringence measurements. However, the agreement between the experimental and calculated curves for dichroism is only qualitative.

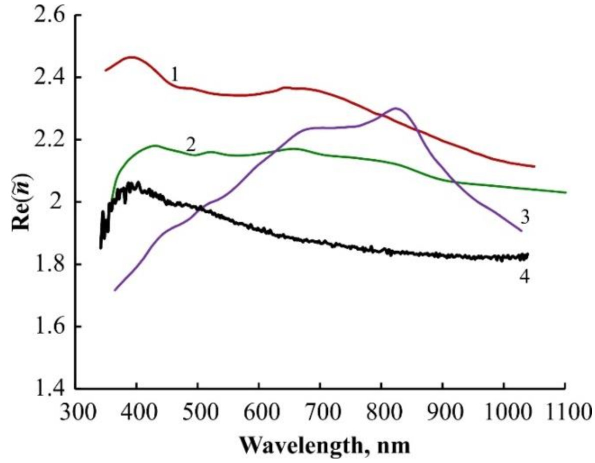

Fig. 6. Spectra of the real part of the refractive index of magnetite, plotted from the known data: 1 – [21], 2 – [22], 3 – [23], 4 – our data for magnetite nanoparticle powder.

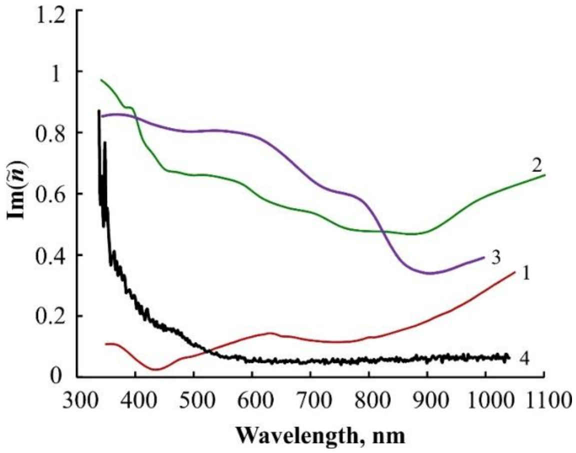

Fig. 7. Spectra of the imaginary part of the refractive index of magnetite, plotted from the known data: 1 – [21], 2 – [22], 3 – [23], 4 – our data for magnetite nanoparticle powder.

The key parameter in (3) and (4) is the dependence of the complex refractive index of magnetite on the wavelength of light $\tilde{n}_m(\lambda) = n_m(\lambda) - i \cdot k_m(\lambda)$. At least 6 spectral dependences of the complex refractive index for magnetite are known in the literature [21-23]. Figures 6 and 7 shows some of these dependencies for real and imaginary parts of refractive index of magnetite. The same graphs show the data obtained by us for the powder of magnetite nanoparticles by the ellipsometric method. It can be seen from the graphs that the spectra of both real and imaginary parts differ significantly. The spread in the values of the real part is from 50% in the short-wavelength part of the visible spectrum to 20% in the near-IR region. The difference in the values of the imaginary part is about 20%. This shows that it is incorrect to use data on optical parameters obtained for macroscopic magnetite crystals to interpret the spectra of magneto-optical effects. A comparison of the experimental and calculated spectra makes it possible to refine the data on the spectral dependence of the real and imaginary parts of the refractive index of nanosized magnetite.

The spectra of the real and imaginary parts of the refractive index of nanosized magnetite can be used to calculate the spectral dependences of the transmission of colloids (Fig. 1). For liquids with a low concentration of particles, to calculate the light extinction, one can use the Rayleigh approximation, which is valid under the condition $x=2\pi a/\lambda<<1$. For such particles, the attenuation cross-section can be written in the form [19]:

$$\sigma_{ext} = \pi a^2 4x \,\mathrm{Im}\left\{ \frac{\tilde{m}^2 - 1}{\tilde{m}^2 + 2}\left[1 + \frac{x^2}{15}\left(\frac{\tilde{m}^2 - 1}{\tilde{m}^2 + 2} \right) \frac{\tilde{m}^4 + 27\tilde{m}^2 + 38}{2\tilde{m}^2 + 3} \right] \right\} + \frac{8}{3} x^4 \,\mathrm{Re}\left\{ \left(\frac{\tilde{m}^2 - 1}{\tilde{m}^2 + 2} \right)^2 \right\}, \tag{5}$$

where $\tilde{m} = \tilde{n}_2 / \tilde{n}_k$ is the relative complex refractive index of the particle material and the dispersion medium.

In Fig. 8 shows a comparison of the experimental transmission spectrum of a weakly concentrated magnetic fluid and calculations by formulas (1) and (5), for which different dependences $\tilde{n}_m(\lambda)$ are used. Calculations show that reasonable agreement with the experiment can be achieved only when using the dependence for the powder of magnetite nanoparticles. To take into account the influence of the dispersion medium of the colloid on the transmission spectra of our samples, we measured the transmission spectra of kerosene. The results were in good agreement with the known data [24].

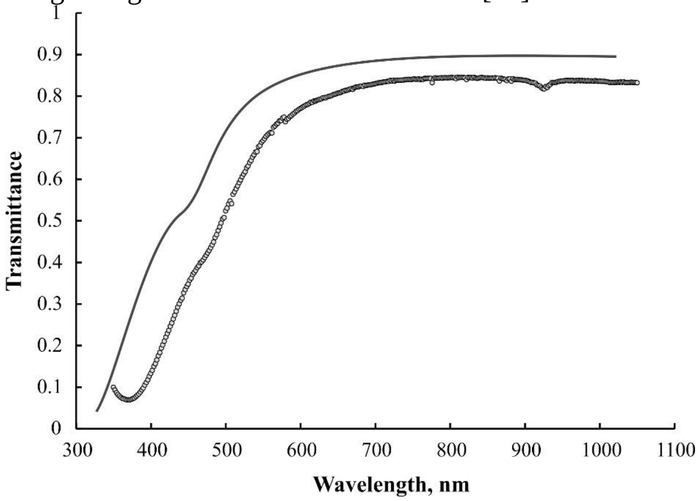

Fig. 8. Calculations of the transmission spectra of a magnetic fluid with a concentration of 0.01% (points - experiment, curve - calculation using the data for powder of magnetite nanoparticles (line 4 on Fig. 6 and Fig. 7).

The transmission spectrum of kerosene does not have any features in the spectral region from 350 to 890 nm. A small absorption band in the near IR region at 890–950 nm is determined by the third overtones of the stretching vibrations of the methyl $–CH_3$ and methylene $–CH_2$ groups. It can be assumed that the transmission spectrum of kerosene does not affect the features of the transmission spectra and spectra of magneto-optical effects in magnetic colloids. The rest of the literature and the results of our experiment on measuring the refractive index of a natural magnetite crystal give transmission spectra that differ significantly from the experimental ones both in the magnitude of the transparency and in the shape of the dependence on the wavelength.

Conclusions

The results of experimental studies of the spectral dependences of birefringence and transparency in magnetic colloids allow us to conclude that the known spectra of the refractive index of bulk magnetite are of little use for quantitative and even qualitative interpretation of optical effects in magnetic fluids based on magnetite. The best agreement with the experiment is obtained from calculations of the magnitudes of optical effects using the experimental spectra of the refractive index of a powder of magnetite nanoparticles. This may indicate that the spectral dependences of the optical parameters of bulk and nanosized magnetite differ significantly. Especially significant is the difference in the imaginary parts of the refractive index, which can reach 2-5 times, depending on the wavelength.

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