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Magneto-optical study of magnetite nanoparticles prepared by chemical and biomineralization process

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ABSTRACT

This paper deals with a magneto-optical study of suspensions of magnetosomes. These magnetosomes are synthesized by biomineralization process of magnetotactic bacteria, followed by steps of isolation and purification in order to obtain stable suspensions. The structural analysis evidences the good crystallinity of the magnetite particles with a diameter of 34 nm. Magneto-induced linear and circular anisotropy confirms the important role played by the chains in the orientation mechanism of such magnetic dipoles. Numerical adjustments of the linear anisotropy curves using a classical Langevin orientation model give the average number of magnetosomes per chain, about 12.

1. Introduction

Magnetic nanoparticles have promising potentials in different fields of applications. They can, for instance, be inserted in a silica matrix to form a composite magneto-optical material that can be easily embedded on integrated optical devices [1]. In the field of biology, magnetic nanoparticles are interesting to realize efficient fluid hyperthermia or drug delivery [2].

Among all the magnetic nanoparticles studied, those prepared by biomineralization process are of particular interest. Magnetotactic bacteria (MTB) are a phylogenetically and morphologically diverse group of microorganisms that can align in and navigate along geomagnetic fields. Each MTB is equipped with one or more chains of a specialized organelle, consisting of a 30–50 nm crystal of iron oxide magnetite or iron sulfide greigite surrounded by a lipid bilayer membrane about 3–4 nm thick [3]. Magnetosome is the intracellular structure that allows MTB to orient in external magnetic field. It consists of a chain of magnetite (and some cases greigite) crystals, each of which is surrounded by a lipid bilayer membrane [4].

Since the pioneer's work of Rosenblatt et al. [5], few works have been led on the magneto-optical properties of magnetosomes. In this paper, we propose to explore some physical and magneto-optical properties of such particles in order to provide a better understanding of their behavior.

Section 1 gives the physical background of magneto-optical effects. Section 2 is concerned with the experiments and a discussion is led in section 3.

2. Magneto-optical background

Numerous materials exhibit linear or circular optical anisotropy under the influence of a magnetic field. These anisotropic media generate two effects: the magneto-optical birefringence and dichroism, which introduce a phase shift Δ and a difference of absorption (related to an angular parameter ψ), respectively, between optical waves polarized along eigenpolarizations of the material. These eigenpolarizations are linear (along orthogonal axis x and y) or circular (along opposite circular senses + and −) for linear or circular anisotropic media, respectively. In the case of a suspension of magnetic nanoparticles in a carrier liquid, an anisotropic linear effect is obtained with a magnetic field direction perpendicular to the light beam (Oz), whereas circular effect needs a longitudinal magnetic field.

Both anisotropic media may be fully characterized by the two ellipsometric angles Δ and ψ linked to the ratio of eigenvalues:

$$\frac{t_x}{t_y}\left(or\ \frac{t_+}{t_-}\right)=\tan\psi\exp(i\Delta) \quad (1)$$

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where $t_{x,y}$ and $t_{+,-}$ are transmission coefficients of linear or circular eigenpolarizations.

For linear effect, one often uses the expression:

$$\Delta n = \frac{\lambda}{2\pi e}\Delta \tag{2a}$$

$$\Delta k = \frac{\lambda}{\pi e}\left(\psi - \frac{\pi}{4}\right) \tag{2b}$$

where e is the sample thickness, λ the wavelength, $\Delta n = n_x - n_y$ is the linear birefringence and $\Delta k = k_x - k_y$ is the linear dichroism.

The anisotropic circular effect is the well-known Faraday effect: a Faraday rotation γ_F associated to a Faraday ellipticity ε_F:

$$\Delta = 2\gamma_F \tag{3a}$$

$$\tan\psi = 1 + 2\varepsilon_F \tag{3b}$$

As these anisotropic media play a role in the behavior of polarized light, the study of the modification of the state of polarization of a linearly polarized light is a way to measure this effect. A full description of these measurements is given by Jamon et al. [6].

Suspensions of magnetic nanoparticles are able to produce these two different effects depending on the orientation of the applied magnetic field. When the magnetic field H is parallel to the laser beam direction, the magnetic moments μ of the particles align along the beam producing the Faraday effect. For an assembly of single nanoparticles the Faraday rotation can be expressed as [7]

$$\gamma_F = \gamma_S \int_0^\infty \Phi(D) L(x(D)) dD \tag{4}$$

with $\Phi(D) = \Phi \frac{D^3 P(D)}{\int_0^\infty D^3 P(D) dD}$ and $x(D) = \frac{\mu H}{k_B T} = \frac{m_S V(D) H}{k_B T}$. The same kind of expression can be also written for ε_F. $L(x)$ is the first Langevin function, Φ the nanoparticles volume fraction of the suspension, D the diameter and $P(D)$ is the log-normal diameter distribution. T and k_B are the temperature and the Boltzmann constant. m_S is the saturated magnetization of the material constituting the nanoparticles. In the case of Magnetite nanoparticles (Fe_3O_4), $m_S = 3.4 \times 10^5$ A/m. γ_s, which depends on the wavelength, is the intrinsic Faraday activity of the particles.

A suspension of magnetic nanoparticles can also produce a linear anisotropy, when it is submitted to a magnetic field, whose direction is perpendicular to the laser beam. This linear anisotropy originates from the alignment of the optical axes of the nanoparticles with the field direction through a rotation of the core body of the particles. This rotation is due to the external magnetic field through an orientation of the magnetic moments of the particles. Indeed, the optical axis of a particle is linked to the magnetic moment through an anisotropy energy E_a [6,8].

The linear birefringence of such an assembly of nanoparticles can, thus, be expressed as [8]

$$\Delta n = \Delta n_S \int_0^\infty \Phi(D)[d\ln(R(\sigma(D)))/d\sigma - 1/3] \times [1 - 3L(x(D))/x(D)] dD \tag{5}$$

Δn_s, which depends on the wavelength, is the intrinsic birefringence of the particles. σ is the anisotropy parameter: $\sigma = E_a/(k_B T)$, and $R(\sigma) = \int_0^1 \exp(\sigma x^2) dx$. The same kind of relation can be written with the linear dichroism Δk. This relation shows that the magnetic field plays a role in the birefringence and dichroism through the second order Langevin term $[1 - 3L(x)/x]$. The anisotropy energy E_a plays a role in the magnitude of the effect: for large anisotropy ($\sigma \gg 1$) the particle behaves as a rigid dipole and $[\mathrm{d}\ln(R(\sigma))d\sigma - 1/3]$ tends to 1, whereas, it tends to zero in the case of superparamagnetic particles ($\sigma \gg 1$) [8].

Relations (4) and (5) show that the behavior of the anisotropic effects as a function of the magnetic field H depends on the mean magnetic moment of the nanoparticles in the suspension through the first and second Langevin functions. The larger the mean magnetic moment, the smaller the magnetic field required to saturate the Langevin functions. Thus, the analysis of the anisotropic effects curves is known to be a way to evaluate the size of the suspended nanoparticles [8]. In our case, it will serve to analyze the chain effects of magnetosomes.

3. Experiments

3.1. Synthesis of magnetite nanoparticles

Bacterial magnetosomes investigated in this contribution were *Magnetospirillum* strain AMB-1. The bacterium was a Gram-negative α-proteobacterium, which is more a oxygen-tolerant bacteria. The medium for *Magnetospirillum sp.* AMB-1 consisted of (per 1 L medium): 10 mL Wolfe's vitamin solution, 5 mL Wolfe's mineral solution, 0.68 g KH_2PO_4, 0.848 g sodium succinate hexahydrate, 0.575 g sodium tartrate dihydrate, 0.083 g sodium acetate trihydrate, 0.225 mL 0.2% (w/v) resazurin (aqueous), 0.17 g $NaNO_3$, 0.04 g ascorbic acid and 2 mL 0.01 M ferric quinate [9]. Resazurin was added to the medium as colorimetric indicator of redox potential. The pH was adjusted to 6.75 with NaOH. This medium was prereduced under nitrogen for a period of 1 h, using copper as a reducing agent, and was subsequently dispersed into culture tubes in an anaerobic hood. Inoculated tubes were incubated at 25 °C for a period of 4 days.

Techniques for the isolation and purification of magnetosome particles from *Magnetospirillum* species are based on magnetic separation [10,11] or a combination of a sucrose-gradient centrifugation and a magnetic separation technique [12]. These procedures leave the surrounding membrane intact and magnetosome preparations are apparently free of contaminating material. Owing to the presence of the enveloping membrane, isolated magnetosome particles form stable, well-dispersed suspensions. After solubilization of the membrane by a detergent, the remaining inorganic crystals tend to agglomerate as a result of magnetic attractive forces.

Typically, 2.6 mg of bacterial magnetite can be derived from a 1000 mL culture of *Magnetospirillum sp.* AMB-1. For the isolation of the magnetosome particles, we have used the modified method described by Grünberg et al. [10]. Approximately 10 g (wet weight) cells of *Magnetotacticum Magnetospirillum* suspended in 100 mL of 20 mM HEPES-4 mM EDTA, pH 7.4, was split up (disrupted) by sonification. The unbroken cells and the cell debris were removed from the sample by centrifugation (10 min, 3036 rpm). The cell extract was placed on a magnet (NdFeB-magnets, 1 h). The black magnetosomes sedimented at the bottom of the tube and the residual contaminating cellular material was retained in the upper part of the tube. The residual contaminating cellular material was decanted. To eliminate the electrostatically bound contamination, the magnetic particles were rinsed first with 50 mL of 10 mM HEPES-200 mM NaCl, pH 7.4, and subsequently with 100 mL of 10 mM HEPES, pH 7.4. After removal of the cell extract from the magnets, the magnetic particles were flushed with 10 mM HEPES buffer. The magnetosomes suspension (black sediment) was then centrifugated (18000 rpm, 30 min at 4 °C). After centrifugation the cell extract was placed on the magnet for 30 min. As before residual contaminating cellular material was retained in the upper part of the tube. The last procedure was repeated ten times to obtain well purified magnetosomes.