Magnetization-induced optical second-harmonic generation and local surface plasmons in magnetic Co$_x$Ag$_{1-x}$ nanogranular films

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Spectroscopy of magnetization-induced second-harmonic generation (MSHG) is studied in magnetic Co$_x$Ag$_{1-x}$ granular films containing Co nanoparticles. A strong resonance of the magnetic contrast of the second-harmonic generation (SHG) intensity is observed in the two-photon energy range from 3.8 eV to 4.5 eV. The local surface plasmons exited in magnetic Co nanogranules in this spectral range assist MSHG and are responsible for a significant enhancement of the SHG magnetic contrast due to the resonances of local optical fields.

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Linear magneto-optics with its more than a century-long history, remains one of the most important experimental methods in studies of magnetism. Meanwhile, significant attention has been recently directed towards the development of nonlinear magneto-optics [1]: magnetization-induced second-harmonic generation (MSHG) was observed experimentally in yttrium-iron-garnet films [2], surfaces of magnetic metals [3], in magnetic multilayers [4] and nanogranules [5]. Experimental measurements [2-5] and theoretical estimates [6] reveal the typical magnitudes of the magnetization-induced effects in second-harmonic generation (SHG): the magnetization-induced variations of the SHG intensity and rotation of the second-harmonic (SH) wave polarization, may exceed the linear magneto-optical Kerr effect (MOKE) by orders of magnitude. The term nonlinear magneto-optical Kerr effect (NOMOKE) is usually used for MSHG in the reflection geometry. As a result of these studies it was recognized that MSHG is a powerful probe of nanomagnetism.

One of the important classes of magnetic nanostructures are magnetic nanogranular films, e.g., Co$_x$Ag$_{1-x}$ films. Below the percolation threshold ($x < 0.45$) Co$_x$Ag$_{1-x}$ films are arrays of Co nanoparticles embedded into nonmagnetic Ag matrix. These Co$_x$Ag$_{1-x}$ granular alloys exhibit giant magnetoresistance effect (GMR) [7].

Apart from extraordinary magneto-transport properties, arrays of magnetic metal nanoparticles are expected to exhibit unusual optical effects, e.g., plasmon assisted linear MOKE is considered in magnetic nanoparticles [8,9]. In this relation, one of the astonishing optical effects in metal nanoparticles is surface-enhanced SHG that was observed by Wokaun, et al. [10] in silver island films. The enhancement of the SHG intensity by up to three orders of magnitude was attributed in Ref. [10] to the resonant enhancement of the local field at the SH wavelength, mediated by the excitation of the local surface plasmons (LSPs) in silver nanoparticles. This plasmon mechanism of the SHG enhancement is profoundly studied for the last decades (see [11] and references in this paper). According to phenomenological approach, second-order nonlinear polarization of an array of small metal particles is given by:

\[
P(2\omega) = L_{\alpha}^2 \chi^{(2)}(2\omega) \mathbf{E}(\omega) \mathbf{E}(\omega),
\]

where $\chi^{(2)}(2\omega)$ is the second-order susceptibility of metal; $\mathbf{E}(\omega)$ is the optical field at fundamental wavelength; $L_{\alpha}^2$ and $L_{\alpha}^2$ are the anisotropic local field (LF) factors at the fundamental and SH wavelengths, respectively, and the symbol ($\hat{\cdot}$) relates to the convolution of the nonlinear susceptibility tensor and vectors of fundamental optical field.

The spectral dependence of the anisotropic LF factor of an array of small metal spheroids embedded in a dielectric matrix, within the dipole and effective media approximations, is given by [12]:

\[
L_{\alpha}(\lambda) = \frac{\varepsilon_d(\lambda)}{\varepsilon_d(\lambda) + \varepsilon_m(\lambda) - \varepsilon_d(\lambda)(N_{\alpha} - \beta x)^2},
\]

where $\varepsilon_d(\lambda)$ and $\varepsilon_m(\lambda)$ are the complex dielectric constants of the dielectric matrix and of the metal at the wavelength $\lambda$, respectively; $\beta$ is Lorenz field factor and $x$ is the filling factor, i.e. the relative fraction of the metal in a composite material; $N_{\alpha}$ is an anisotropic shape-dependent depolarization factor of the spheroids; subscript $\alpha = ||, \perp$ denotes the tangential and normal orientation of principle semiaxes $a$ and $b$ of the spheroids with respect to the sample surface (see the left-hand inset in Figure 1b).

The resonant wavelength of the LF factor, $\lambda_{res}$, corresponds to setting the real part of the denominator in Eq. 1 to zero. The resonant increase of the LF factor at $\omega$ or $2\omega$ results in a many-fold increase of the nonlinear-optical response of a nanoparticle array.

In this Letter, MSHG assisted by excitation of local surface plasmons is studied in Co$_x$Ag$_{1-x}$ nanogranular films. For the Co concentration $x < 0.45$ these films consist of Co nanoparticles embedded into Ag matrix. It turns out, that the excitation of local surface plasmons at
the SH wavelength in this nonmagnetic composite material results in a resonant behavior of the SHG magnetic contrast.

In the phenomenological description of MSHG [1], the second-order susceptibility of a magnetic material is considered as a combination of crystallographic (nonmagnetic) and magnetic terms, which possess even and odd parities in magnetization, $M$, respectively: 

$$\chi_{ijk}^{(2)} = \chi_{ijk}^{(2)\text{cryst}} + \chi_{ijk}^{(2)\text{odd}}(M), \quad \chi_{ijk}^{(2)\text{cryst}} = \chi_{\parallel \parallel \parallel}^{(2)},$$

where $\chi_{ijk}^{(2)\text{cryst}}$ is the crystallographic nonmagnetic susceptibility and $\chi_{ijk}^{(2)\text{odd}}(M)$ is the magnetic susceptibility.

Nonmagnetic susceptibility is a conventional tensor whereas the magnetic susceptibility is a pseudotensor. As a consequence, these susceptibilities possess different sets of tensor elements for the materials of the same crystallographic symmetry. These tensor elements of the corresponding susceptibilities are shown in Table 1 for the in-plane isotropic media.

The intensity of MSHG, which is assisted by local plasmon excitation at the SH wavelength, is given by:

$$I_{2\omega}(M) \sim \left| E_{2\omega}^{\text{cryst}} + E_{2\omega}^{\text{odd}}(M) \right|^2 \sim \left| \sum_{\alpha} \left( I_{2\omega}^{\alpha}(\chi_{\alpha \alpha \alpha}^{(2)\text{cryst}} + \chi_{\alpha \alpha \alpha}^{(2)\text{odd}}(M)) f_i E_i f_j E_j f_k E_k + c.c. \right) \right|^2,$$

where $E_i$ is the $i$th component of the fundamental field, $E_{2\omega}^{\text{cryst}}$ and $E_{2\omega}^{\text{odd}}(M)$ are the SH fields originating from the crystallographic and magnetic susceptibility, respectively, and $f_i$, $f_j$, $f_k$ are coefficients that contain Fresnel factors and linear magneto-optical rotation of polarization of the fundamental field. The first subscript of tensor elements $\chi_{ijk}^{(2)}$ is denoted as $\alpha = \parallel, \perp$, attributing to the corresponding components of the anisotropic LF factor at the SH wavelength.

Magnetization-induced effects in the SHG are described by the magnetic contrast:

$$\rho = \frac{I_{2\omega}(M \uparrow) - I_{2\omega}(M \downarrow)}{I_{2\omega}(M \uparrow) + I_{2\omega}(M \downarrow)},$$

where $I_{2\omega}(M \uparrow)$ and $I_{2\omega}(M \downarrow)$ are the values of the SHG intensity for the opposite directions of the magnetization.

The samples of magnetic nanogranular Co$_x$Ag$_{1-x}$ films are prepared by the co-evaporation of Co and Ag from two independent electron-beam sources onto glass-ceramic substrates. The structure of Co$_x$Ag$_{1-x}$ films is characterized by X-ray diffraction and reveals the existence of nanogranules with the diameter ranging from 3 nm to 6 nm for the composition $x < 0.4$. The fabricated granular films exhibit the GMR effect up to 16% at room temperature [13].

The output of an optical-parametric-oscillator (OPO) system "Spectra-Physics 710" with tuning range of wavelength from 730 nm to 1000 nm, pulse duration of 4 ns, pulse intensity of 2 MW/cm$^2$, and a Q-switched YAG:Nd$^{3+}$ laser at 1064 nm wavelength, pulse duration of 15 ns and pulse intensity of 1 MW/cm$^2$ are used as the fundamental radiation. The SHG radiation reflected from the sample is filtered out by appropriate glass band-pass and interference filters and is detected by a photomultiplier tube and gated electronics. To normalize the SHG signal over the OPO and YAG:Nd$^{3+}$ laser fluency and the spectral sensitivity of the optical detection system, an independent reference arm is used with a Z-cut quartz plate as a reference and a detection system identical to that in the "sample" arm.

An in-plane dc-magnetic field up to 2 kOe provided by permanent Fe-Nd-B magnets is applied to the samples in nonlinear magneto-optical measurements.

The relative phase of $E_{2\omega}^{\text{odd}}(M)$ and $E_{2\omega}^{\text{cryst}}$ is measured by the nonlinear optical interferometry method described in details elsewhere [14]. The experimental scheme of the nonlinear optical interferometry is shown in the inset of Figure 2b. The SH fields from the sample and the interference interfere at the photomultiplier while the reference SHG source is translated along the direction of the fundamental beam. The SHG interferometry is performed by translating a 30 nm thick indium-tin-oxide (ITO) film on a glass substrate. The interference pattern, i.e., an oscillating dependence of the SHG intensity as a function of the reference displacement, results from the phase shift between the interfering SH fields from the sample and the reference. Magnetization-induced shift $\theta(M)$ between interference patterns, which appears due to the reversal of $M$, is shown on vectorial diagram in the bottom inset of Figure 1a. This diagram also shows a phase shift $\Psi(M)$ between $E_{2\omega}^{\text{odd}}(M)$ and $E_{2\omega}^{\text{cryst}}$.

To study wavelength dependence of $\rho$, spectral dependencies of the SHG intensity are measured for p-in,p-out combination of polarizations of the fundamental and SH waves for two opposite directions of $M$ in the configuration of the transversal NOMOKE (see the top inset of Figure 1a). Figure 1a shows the experimental spectra of $\rho$ in Co$_x$Ag$_{1-x}$ films with $x=0.24, 0.35, 0.41$. All spectra of the SHG magnetic contrast demonstrate pronounced
Resonances in the SHG intensity and the resonance of the SHG magnetic contrast demonstrate significant enhancement (by more than one order of magnitude) of both nonmagnetic SHG and the relative magnetic contribution. Inset in Figure 1b shows optical spectra of bulk Co in corresponding spectral range that reveal monotonic feature-less behavior of the dielectric constant [15]. The lack of resonant features in optical spectra of Co implies that resonances of the SHG magnetic contrast and the SHG intensity are not associated with the bulk magnetooptical and nonlinear optical properties of Co. Optical properties of metal nanoparticles embedded to matrix with dielectric constant $\varepsilon > 0$ exhibit additional resonances related to LSPs [16]. Inset in Figure 1b shows that dielectric constant of Ag is positive in considered spectral range of two-photon energy from 3.8 eV to 4.5 eV [15]. This implies that in the aforementioned spectral range one can expect the appearance of LSP features in optical spectra. Particularly these LSP modes can be responsible for the resonances of $L^2_\omega$ and corresponding resonances in the spectra of the nonmagnetic SHG intensity shown in Figure 1b.

We attribute these resonances to the excitation the LSP modes in Co nanogranules at the SH wavelength. The split of the LSP modes in the spectral doublet is caused by the deviation of the shape of Co nanoparticles from spheres [17]. Relation of the resonant features of the SHG spectra to the LSP modes verifies also by the dependence of the resonant wavelengths $\lambda_{res}$ on Co concentration. Increase of $x$ results in the increase of the interparticle dipole-dipole interaction and red-shift of the LSP resonant wavelengths which is apparently seen in the set of the SHG spectra in Figure 1b.

Comparison of the magnetic and nonmagnetic spectra shows that the resonant wavelength of the SHG magnetic contrast in Figure 1a is close to the wavelength of the split between the LSP resonances at nonmagnetic SHG spectra in Figure 1b. As both crystallographic and magnetic susceptibilities of bulk Co are not supposed to possess a resonant behavior in the considered spectral range, the resonance in the magnetic contrast spectra can be explained by the contribution to the nonlinear optical response from resonances of the LF factor corresponding to the LSP modes.

The models, which are considered for the LF factor and NOMOKE with the LSP assistance, are used for the approximation of the experimental spectroscopic results. Solid lines in Figure 1b are the result of the approximation of the nonmagnetic SHG spectra with Eqs. 1 and 2, that take into account spectral dependence of $L^2_\omega$. Approximation of the set of spectra for variations of Co content shows that spectral features of nonmagnetic SHG can be attributed to the resonances of $L^2_\omega$. Two trends in the nonmagnetic SHG spectra red-shift of the resonant wavelength and the decrease of the resonant amplitude for the decrease of the Co content, correspond to the conclusions of the LSP assistance due to the local field factors. The major adjusting parameter of the ap-

![Graph of spectral dependencies of the SHG magnetic contrast for Co$_x$Ag$_{1-x}$ films with $x=0.24, 0.35, 0.41$; top inset: geometry of transversal NOMOKE; bottom inset: vectorial diagram for SH fields, measured for opposite directions of magnetization and corresponding magnetic and nonmagnetic contributions to the SH field; b) spectral dependencies of the nonmagnetic SHG intensity for Co$_x$Ag$_{1-x}$ films with $x=0.1, 0.17, 0.35$; left-hand inset: schematic of nanogranular film; right-hand inset: spectra of dielectric constants for Co and Ag (from Ref. [15]).]
proximation is the ratio of spheroid semiaxes \( a/b \). The complete set of nonmagnetic SHG spectra with variations of \( x \) from 0.1 to 0.41 is well approximated with the same value of \( a/b = 0.5 \pm 0.1 \), that is a strong argument for the correctness of the plasmon model in the case of Co\(_{0.35}\)Ag\(_{0.65}\) granular films.

For the explanation of the spectral behavior of the SHG magnetic contrast, a simple model is developed which takes into account the assistance of NOMOKE in granular films by local surface plasmons in magnetic nanoparticles. In this model we consider Co\(_x\)Ag\(_{1-x}\) granular film as a three-dimensional array of small Co spheroids with semiaxes \( a \) and \( b \) parallel and perpendicular to the surface, respectively, embedded in Ag matrix (see the left-hand inset in Figure 1b). We suppose that a plasmon resonance is achieved at the SH wavelength and complex anisotropic LF factors are \( L_{\omega} = C_\alpha \exp^{-\omega \varphi_\alpha} \), where \( C_\alpha \) and \( \varphi_\alpha \) are real amplitude and phase of the anisotropic LF factor, respectively. From the symmetry analysis summarized in Table 1 one can suppose that the predominant first subscript for the elements of the magnetic susceptibility of the in-plane isotropic film is \( \alpha = \parallel \) whereas \( \alpha = \perp \) is predominant as a first subscript for the elements of the nonmagnetic susceptibility. Together with the assumption that \( \chi_{\parallel jk}^{(2)}(M) \gg \chi_{\perp jk}^{(2)}(M) \), the MSHG magnetic contrast for the case of the LSP assistance is given by:

\[
\rho \sim \sum_{j,k} \frac{\chi_{\parallel jk}^{(2)}(M)C_\parallel}{\chi_{\perp jk}^{(2)}C_\perp} \times \cos[\varphi_\perp - \varphi_\parallel + \Phi(M)],
\]

where \( \Phi(M) \) is the relative phase between \( E_{2\omega}^{\parallel}(M) \) and complex LF factor \( L_{\omega}^{\parallel} \) as this is shown on the vectorial diagram in the inset of Figure 2a. The first subscripts of tensor elements \( \chi_{\parallel jk}^{(2)} \) are denoted as \( \parallel \) and \( \perp \) to be attributed to corresponding components of the anisotropic LF factor.

Using this model, the mechanism of the spectral dependence of the SHG magnetic contrast can be described. In fact, the model approximation of nonmagnetic SHG spectra gives numerical results for the spectral dependencies of the amplitudes and relative phase of local field factors, \( \Delta \varphi = (\varphi_\perp - \varphi_\parallel) \), in the spectral range of the LSP modes (see vectorial diagram at inset in Figure 2a). In turn, these data together with experimental data on the spectral dependence of the SHG magnetic contrast allow one to calculate, on the base of Eq. 4, spectral dependencies of the magnetic, \( \Phi(M) \), and nonmagnetic, \( \Delta \varphi = (\varphi_\perp - \varphi_\parallel) \), phases. Figure 2a shows these spectra for Co\(_{0.35}\)Ag\(_{0.65}\) film that demonstrate resonance spectral dependence of the nonmagnetic phase and spectral independent behavior of the magnetic phase. Spectral dependence of the nonmagnetic phase shows a good qualitative agreement with the spectrum of the SHG magnetic contrast. Moreover, for off-resonance conditions, the magnetic phases \( \Phi(M) \) and \( \Psi(M) \) should coincide, which can be checked by the SHG interferometry. Figure 2b shows the row interference patterns for the opposite directions of M in Co\(_{0.35}\)Ag\(_{0.65}\) film that demonstrate a clear magnetic shift of the phase \( \theta(M) = 8^\circ \) of SH field. The value of \( \Psi(M) = 40^\circ \pm 10^\circ \) extracted from the shift of interferometric patterns is in satisfactory agreement with results of calculation for the resonant spectral range in Figure 2a. Thus, the qualitative agreement between spectral dependencies of \( \rho \) and \( \Delta \varphi \) and approximate equality of \( \Phi(M) \) and \( \Psi(M) \) allow one to associate the resonances in nonlinear magneto-optical response of Co\(_x\)Ag\(_{1-x}\) films with the assistance from LSP modes exited in magnetic nanograins.
In conclusion, local surface plasmons are observed in magnetic all-metal Co$_x$Ag$_{1-x}$ nanogranular films. The excitation of local surface plasmons in magnetic Co nanoparticles mediates magnetization-induced SHG resulting in a strong resonance increase of both the MSHG magnetic contrast and the SHG intensity. This enhancement of MSHG in magnetic nanoparticles is due to the assistance of the nonlinear optical effect from the LSP modes and of a coherent (phase-dependent) interference of magnetic and nonmagnetic contributions to the SH fields.

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