Enhanced Magneto-Optics and Size Effects in Ferromagnetic Nanowire Arrays**

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Localized surface plasmons are under intensive study since long ago because they play a very important role in the optical properties of metallic systems. In particular, they become especially relevant in the optical properties of nanostructures, such as tiny particles embedded in dielectric matrices. These localized modes appear due to the dielectric contrast between the metal and the host, the real part of the dielectric constant of the metal is negative whereas that of the dielectric matrix is positive, and they are the origin of the optical resonances observed in these systems. The intensity as well as the spectral position of these resonances strongly depends on a variety of parameters such as the size, the shape, the concentration of the metallic particles or the refractive index of the matrix. The vast majority of the studies have been so far devoted to study gold or silver metal particles since their free electron contribution to the optical properties in the infrared and visible spectral range is predominant, exhibiting also a low damping constant. In other metals such as palladium, platinum, cobalt, nickel or iron, the free electron contribution to the optical properties is smaller than for Au or Ag, and have a higher damping constant, therefore their surface plasmon resonances appear broader and less defined. On the other hand, some of these metals like Fe, Co and Ni, possess spontaneous magnetization which enables them to present magneto-optical properties, which are absent in noble metals. This characteristic can be used to design new kind of plasmonic structures. For example, very recently a new type of plasmon-resonance-like biosensor based on the combination of Co and Au continuous layers has been developed. This device exhibits a higher sensitivity than that of the conventional Surface Plasmon Resonance (SPR) biosensor. Moreover, different theoretical works have suggested that surface plasmon resonance of magnetic metallic nanoparticles could enhance the magneto-optical activity with respect to that of a continuous medium. In these works the size of the nanoparticles under consideration is always much smaller than the wavelength of light and in all but in Ref. [9] the interaction between the particles was not considered. But the particle size and the radiative coupling between nanoparticles strongly modifies the optical properties of the system and, therefore, it may also modify its magneto-optical response. This is precisely the scope of this work, where we analyze the dependence of the magneto-optical properties on the size and on the dielectric environment of a system consisting on Ni nanowires embedded in an alumina matrix. This system has already shown to exhibit interesting effects, such as an enhancement of the magneto-optical Kerr rotation, whose origin will be pointed out here. We will show that the enhancement is due to a surface plasmon resonance of the Ni nanowires, its spectral position depending on the wire diameter. In addition, the Kerr effect rotation spectrum is shown to strongly depend on the local dielectric environment.

The samples used in this work are hexagonal arrays of nickel embedded in alumina membranes (5 μm thick) obtained by anodization of aluminium foils. For the synthesis of ordered alumina membranes we have used two different approaches. In the first one, the samples with smaller pore diameter have been obtained via a two-step electrochemical process. Pores with a typical diameter of 40 nm self arrange during the first anodization process into hexagonal ordering with lattice constant of around 105 nm, where the size of the ordered regions are about 2.5 μm. In order to obtain monodomain samples with a perfect ordering of the pores we have employed nanoimprint lithography. This prepatterned aluminium foil was subsequently anodized and, controlling the anodization conditions, a perfectly ordered hexagonal array of pores with a pore diameter of 180 nm approximately and interpore distance of about 500 nm was obtained. In Ref. [17] it has been shown that the refractive index of the alumina electrochemically obtained is not uniform in the lateral direction being smaller when closer to the holes, being the shell of the order of 50 nm for an alumina matrix with 180 nm holes and
500 nm pitch. In order to obtain a magneto-optically active sample the pores are electrochemically infiltrated with nickel by pulsed electrodeposition, obtaining two different samples one with 40 nm diameter nickel wires (sample A from now on) and another with 180 nm diameter nickel wires (sample B from now on). Figure 1a shows a SEM image of sample A and Figure 1b that corresponding to sample B where the 50 nm shell is clearly visible. Conceptually, magneto-activity arises from the fact that the dielectric tensor of the material is no longer diagonal in presence of a magnetic field (B). Depending on the orientation of the magnetic field with respect to the sample surface and to the incidence plane of the light, there will be only some non-zero off-diagonal elements. Throughout this paper we will restrict ourselves to normal incidence and to the so-called polar configuration where $B$ is perpendicular to the sample plane and parallel to the incidence plane (see sketch in Fig. 1). The dielectric tensor then reads as follows:

$$
\begin{align*}
\begin{bmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & 0 \\
\varepsilon_{xy} & \varepsilon_{yy} & 0 \\
0 & 0 & \varepsilon_{zz}
\end{bmatrix}
\end{align*}
$$

The presence of the non-zero off-diagonal element makes the polarization plane of both the reflected and the transmitted light to be rotated with respect to that of the incident one. In our case we will restrict ourselves to the analysis of the polarization plane of the reflected light (Kerr rotation).

In Figure 2 we show the Kerr rotation spectra corresponding to the two samples of Figure 1. The symbols in (a) represent the experimental Kerr rotation for sample A whereas those in (b) are for sample B. The continuous lines represent the Kerr rotation for a film of bulk Ni with optical constants taken from Ref. [18] and magneto-optical constants $\varepsilon_{xy}$ taken from [19]. In Figure 2a we can distinguish two different spectral regimes, one below 2.5 eV and the other above than 2.5 eV. In the low energy regime the Kerr rotation is, as it would be expected, smaller than that of nickel bulk. However, beyond that point the Kerr rotation is equivalent (the negative sign only states for the direction of the rotation, clockwise (counter clockwise) positive (negative)) for the nanostructured sample, meaning that for this energy range it is possible to obtain a big effect despite having a smaller amount of magneto-optically active material. In order to unravel the origin of this enhancement we analyze sample B, in which the concentration of magneto-optically active material is very close to the first one, but the diameter of the nanowires is larger. The results are depicted in Figure 2b and we can see how the signal is significantly smaller than for Ni bulk, in this case being the nanostructure-to-bulk ratio in close relation with the nickel percentage.

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**Figure 1.** SEM images of hexagonal arrays of nickel nanowires embedded in an alumina matrix. In (a) the nanowire diameter is $d=40$ nm and the interwire distance $a=105$ nm and in (b) $d=180$ nm and the interwire distance $a=500$ nm. The 50 nm inner shell where the refractive index of alumina is slightly smaller is clearly visible. Bottom: schematic representation of the incident linearly polarized light over a slab of thickness $h$, with a hexagonal array of ferromagnetic wires of diameter $d$ and lattice parameter $a$. The direction of the magnetic field is perpendicular to the sample plane and the outgoing reflected wave has its polarization rotated and slightly elliptical.

**Figure 2.** a) Kerr rotation spectrum of an array of nanowires with $d=40$ nm and $a=105$ nm. The continuous line represents the Kerr rotation of nickel bulk. The enhancement of the rotation around 3 eV is clearly visible. The dashed line is the SMM calculation. b) The same as in (a) but the nanowire diameter is $d=180$ and the lattice constant $a=500$ nm.
The differences arising from the two samples indicate that the Kerr spectrum strongly depends on the diameter and separation of the motives. In order to theoretically analyze the enhancement and its characteristics we are going to employ a Scattering Matrix Method (SMM) adapted to be able to consider magneto-optical effects\textsuperscript{20} to describe the wave propagation along the nanostructured material. This method allows an exact solution of the wave propagation, taking into account all possible interactions among the different wires of the ordered array, allowing us to calculate the full reflectivity matrix \((s\text{ and} \ p, \text{are the two polarizations}):\)

From that we can obtain the complex Kerr rotation, that is defined as \(\phi = \theta + i\varphi = r_{ps}/r_{pp}, \text{being} \ \theta \text{the Kerr rotation and} \ \varphi \text{the Kerr ellipticity.}

\[
\varepsilon = \begin{pmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & 0 \\
-\varepsilon_{xy} & \varepsilon_{yy} & 0 \\
0 & 0 & \varepsilon_{zz}
\end{pmatrix}.
\]

In Figure 2 (dashed lines) we can see the results of applying the SMM to the two different structures studied experimentally, i.e., a hexagonal array of Ni wires embedded in an alumina matrix. The dashed curve in Figure 2a is the result of considering the nickel wires to be embedded in a \(n = 1.7\) dielectric environment with a 20 nm shell of \(n = 1.6\). In Figure 2b the core–shell is of 50 nm. As it can be seen the agreement is qualitatively very good for both cases, although a better quantitative agreement is reached in the case of sample A.

The behaviour of the Kerr spectra suggests a red shift of the structure appearing at 3.1 eV in Figure 2a when the diameter of the wires increases. This suggests that such a structure might have a plasmonic origin. To shed some light on this we present in Figure 3a and b the result of numerical simulations for the Kerr spectra of nickel wires of different diameters, namely 40, 80, and 125 nanometers, adjusting the lattice parameter so that the nickel concentration remains constant, i.e., 90, 180, 281 nanometers respectively, in two different backgrounds: alumina (a) with \(n = 1.7\) and air (b) with \(n = 1.0\). These simulations reveal that, for both environments, the structure experiments a red-shift when the diameter of the wires increases. In the case of Ni nanowires embedded in air, the feature is located in the ultraviolet energy range, shifting from 3.6 eV to 3.2 eV as we increase the diameter from 40 nm to 125 nm. Furthermore, when the matrix is alumina, the energy position is lower than that for the same diameter wires in air, indicating also a red-shift as a function of the refractive index of the environment. In addition, despite the fact that the amount of Ni in the nanowire layers is only about 18%, the intensity of the Kerr rotation of the system is either similar (alumina matrix) or even larger (air matrix) than that of a continuous Ni film. The difference in the intensity of the rotation for the two matrices is due to a pure optical effect coming from a reduction of \(r_{pp}\). All these facts reinforce the suggestion of a plasmon-like behaviour.

\[
\begin{pmatrix}
 r_{ss} & r_{sp} \\
 r_{ps} & r_{pp}
\end{pmatrix}
\]

Figure 3. Theoretical Kerr rotation spectra for arrays of nickel nanowires with different diameters. The lattice parameter has been adjusted to keep the nickel concentration constant. In (a) the wires are embedded in alumina whereas in (b) the host material is air. The spectra appear red-shifted as the diameter of the wires increases. This red-shift also occurs for wires of equivalent diameter when the refractive index of the host increases. Despite that the nickel concentration is always around 18% the rotation is of the order (alumina) or even higher (air) than that of the bulk material.

To get a deeper insight we are going to compare the results described above with the well known results for homogeneous layers. In that kind of system the optical properties can be understood through the study of the complex refractive index \((n, \ k)\). In particular, plasmonic structures manifest themselves as a peak in the spectrum of \(k\). In our case, the material is not homogeneous; therefore we need to define an effective homogeneous medium so that an effective pair of values of \(n\) and \(k\) can be obtained. The values of \(n\) and \(k\) for such an effective complex refractive index are calculated from the theoretical values of the transmission and the reflection coefficients. The results are depicted in Figure 4, where we show the effective \(k\) and its evolution as a function of the diameter for nickel wires embedded in air (a) and in alumina (b). As we can see, all the spectra show a peak, which can be related to a plasmonic structure, and the behaviour found in the analysis of the Kerr rotation finds a clear correspondence here. The peak position red-shifts when the diameter of the wires increases, irrespective of the refractive index of the host material. Also, for equivalent diameters, the peak in \(k\) appears red-shifted for the host with the highest refractive index. The effect of the refractive index of the matrix also affects the absolute value of \(k\), appearing higher in the case of the alumina matrix. This is due to the stronger localization of the plasmon that propagates along the wires, which makes the travelling wave to “probe” a larger amount of nickel and thus to gather more ab-
Figure 4. a) and b) Effective absorption constant for the same systems as in Figure 3. The evolution of the peak nicely reflects that observed in the Kerr rotation spectra. In (c) and (d) we have plotted the ratio of magneto-optical activity (see text) between the nanowire system and the bulk material, both for nanowires in air (c) and in alumina (d). The peaked structures shown in (c, d) reproduce that of the effective \( k \), indicating the origin of the red-shift and of the enhancement. Panels (e) and (f) contain the purely magneto-optical part of the magneto-optical activity, where it can be seen that with an 18% of the material the values are of the order of 60% of that of Ni bulk.

The Kerr rotation has two components: \( r_{pp} \) that accounts for the pure magneto-optical effect, and \( r_{pp} \) which is a purely optical effect. In this case the relative intensity goes in the opposite direction as in (a) and (b), which is originated from the aforementioned reduction of the optical part of \( \phi \) (relative) in the case of an air environment with respect to that of alumina. To point out that the enhancement does not arise from a purely optical effect we present in Figure 4c and f the purely magneto-optical part. The shape is again very close to that of \( k \) since the origin is the same, i.e., the presence of the plasma. The value of \( |r_{pp}| \) for an 18% of Ni is of the order of 60% of that corresponding to Ni bulk. This represents an enhancement of the polarization conversion resulting from the larger “probing” of the nickel wire due to the localization of the plasmon.

To sum up, we have fabricated a nanostructured material, composed of hexagonally arranged ferromagnetic nanowires, characterized and carefully analyzed its magneto-optical response. We have found that this material exhibits an enhancement of the Kerr rotation, as well as a strong dependence on the nanowire diameter, maintaining the concentration constant. Based on extensive numerical simulations, we have explored the origin of the enhancement and of the structure of the Kerr rotation. The origin is found to be fully compatible with a plasmon-like structure that propagates along the ferromagnetic wires.

**Experimental**

Both ordered polydomain and monodomain alumina membranes are obtained from high purity (99.999%) aluminium foils which are decreased in acetone and cleaned in a mixed solution of HF:HNO\(_3\):H\(_2\)O\(_3\)=1:10:20:69. Subsequently, the aluminium is annealed under nitrogen ambient at 400 °C for 3 h for the polydomain sample. To reduce the mean roughness of the surface, both samples are electropolished in a 25:75 volume mixture of HClO\(_4\) and H\(_2\)SO\(_4\).

**Preparation of Ordered Polydomain Alumina Membranes:** Here, so-called hard imprint lithography is employed for pre-patternning of the aluminium surface. The master stamp consists of Si\(_3\)N\(_4\) pyramids with height of 260 nm and a lattice constant of 500 nm water bonded to a 4 in. silicon substrate and its fabrication process is described in details in ref. [21]. The stamp with the size of \( 5 \times 5 \) mm\(^2\) is placed on electrochemical polished AI. The pattern on the master stamp is transferred onto the surface of Al under 5 kN cm\(^{-2}\) with an oil press (PW, Paul-Otto Weber GmbH, Germany). The pre-patterned aluminium foil is anodized in 1 wt % phosphoric acid solution at 195 V for 1 h. Ordered alumina nanopores arrays is obtained with a 180 nm pore diameter distribution, an interpore distance of 500 nm and a thickness of \( \approx 5 \mu m \).

**Preparation of Ordered Monodomain Alumina Membranes:** Here, grown inside the pores of both kind of samples using the same electro-deposition process. First of all, the barrier layer at the bottom of the pores is thinned by several voltage anodization steps. Stepwise the applied anodization potential is reduced until a barrier layer thickness of the alumina template of less than 7 nm is reached \((=5 \, V)\). Using pulsed electrodeposition, the porous alumina membranes are homogeneously filled. Nickel is deposited from a highly concentrate Watts-Bath electrolyte \((300 \, g \, L^{-1} \, NiSO_4 \cdot 6H_2O, \, 45 \, g \, L^{-1} \, NaCl, \, H_2O, \, 45 \, g \, L^{-1} \, H_2BO_3, \, pH=4.5, \, T=35^\circ \)C). The experimental details of the pulsed electro-deposition process are described in ref. [2]. To characterize the metal-filled template, the top of the alumina membrane is fixed to a silicon substrate by an epoxy glue. Next, the aluminium substrate is removed by a saturated HgCl solution and the structure is turned up-side down. The barrier layer and the dendritic pore structure of the filled template are removed by a focused ion beam. Then, the top ends of the nanowires became visible at the surface and a relatively smooth surface is obtained.

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