Magnetization-induced chirality in second harmonic generation response of U-shaped permalloy nanostructures

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Magnetization-induced circular dichroism (CD) in optical second harmonic generation (SHG) is observed in planar symmetrical arrays of U-shaped permalloy nanostructures. We demonstrate that extrinsic chirality of an array leads to the CD effect that strongly depends on the azimuthal orientation of the sample. In the absence of magnetization, the value of the SHG CD effect averaged over 2π azimuthal angle is zero, while up to 6% averaged SHG CD appears as the dc magnetic field is applied along the symmetry axis of the structure. Importantly the averaged SHG CD effect changes its sign under the reversal of the magnetic field, which corresponds to the appearance of magnetization driven true chirality in an array of symmetric magnetic nanostructures.

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I. INTRODUCTION

Design of functional metamaterials for efficient control and conversion of the main parameters of optical radiation such as polarization, spectrum, phase, and intensity is an actual task nowadays. Recent progress in this area is determined presumably by the development of precision methods for the creation of nano- and microstructured materials and metasurfaces that reveal unusual properties in the interaction with optical radiation [1–3]. Therefore, the search for promising approaches and scientific principles for the production of metamaterials that demonstrate high optical activity, nonlinear and magneto-optical response, as well as a comprehensive study of their properties is an important problem.

Chiral planar metamaterials that by definition lack mirror planes among the set of their symmetry elements [4] are promising objects demonstrating optical activity, which appears as rotation of the polarization plane of the incident radiation and circular dichroism effects. The design of such structures, namely the constituting material, shape, size [5–7], and mutual arrangement of individual elements in an array [8–10], as well as the properties of the substrate, plays a decisive role in the formation of their optical spectra. Linear optical circular dichroism (CD), i.e., the difference in absorption coefficients for the left and right circularly polarized electromagnetic waves, was detected in chiral structures of various designs, such as fish-net [6], gold gammadions [11], and "split-ring" resonators [5]. It was recognized that for the case of such metasurfaces CD effect appears due to different distribution of optical local field within nanoelements for various circular or linear polarizations of the probing light, which leads to the difference in their absorption or refraction.

Nonlinear optical effects and in particular optical second harmonic generation (SHG) was studied in arrays of L-shaped [12], sawtooth [13], G-shaped [14–16], and other types of 2D chiral nanoelements [17]. It was shown that besides the CD effect in the SHG response that is much higher as compared to the linear optical case, new chirality-driven phenomena appear, such as SHG asymmetry [14] and inverse dichroism effect in SHG [18]. Higher values of the chirality-induced SHG effects are due to the nonlinear dependence of the SHG intensity on the local field at the fundamental wavelength, which is sensitive to the handedness of the structure.

One more interesting aspect was recognized by the authors of Refs. [19,20]: Optical activity can appear in arrays of achiral structures due to the so-called extrinsic chirality, which appears at oblique incidence for certain azimuthal orientations of a metasurface when the mirror symmetry is absent [21–23]. In this case the SHG asymmetry as well as the CD effect were demonstrated, while their values came to zero when being integrated over all the azimuthal orientation of the structure.

The range of unique properties of chiral structures can be extended if a possibility for the additional control of optical activity in their optical and nonlinear optical response is realized. In this paper we demonstrate such a possibility by applying external *dc* magnetic field to a metasurface built of achiral magnetic nanoelements. The experiments are performed for a rectangular array of permalloy U-shaped nanostructures, and the CD effect in reflected SHG is analyzed. We show that under magnetization-induced breaking of the time-reversal symmetry, such a metasurface reveals chiral behavior visualized by the SHG CD effect.

II. SAMPLES AND EXPERIMENTAL SETUP

We studied arrays of permalloy ($Ni_{80}Fe_{20}$) U-shaped nanostructures. Nanoelements (0.52 μm × 0.66 μm, thickness 50 nm) are arranged in an rectangular array with the period of about 1 μm made on a silicon (100) substrate using deep ultraviolet lithography (DUV) at 248 nm exposure wavelength, followed by electron beam evaporation and ultrasonic

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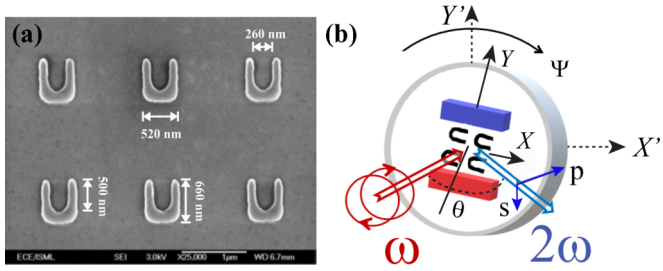

FIG. 1. (a) SEM image of the sample under study; (b) scheme of the SHG experiment.

assisted liftoff process in OK73 resist thinner. The SEM image of the sample is shown in Fig. 1(a). Details of the fabrication process are described elsewhere [24]. Importantly such a planar array of U-shaped nanostructures is achiral, as it has a mirror plane perpendicular to its surface, so it should not reveal CD effect in the absence of magnetization, while extrinsic chirality should be observed. As a reference, a continuous 50 nm thick permalloy film was deposited on a silicon substrate.

In the SHG experiments, a Ti:Sapphire laser operating at the wavelength of 790 nm, pulse width of 100 fs, repetition rate 80 MHz, and the average intensity of 40 mW was used as the source of the fundamental radiation [Fig. 1(b)]. The laser beam was focused on the sample into a spot of approximately 50 μm in diameter, thus over 700 U-shaped elements were irradiated simultaneously. This allowed for effective SHG averaging over the array of U-shaped nanoelements and elucidation of the effect of imperfections of the shape and periodicity of distribution of nanostructures. We analyzed the parameters of the second harmonic radiation that was specularly reflected from the sample, for the two angles of incidence of the fundamental beam $\theta = 20^\circ, 40^\circ$.

For the study of the CD effect in the second harmonic, the intensity of s or p linearly polarized SHG was measured for the *left* or *right* circular polarizations of the fundamental beam and the CD value in SHG was calculated as:

$$CD_p = \frac{I_p^{right} - I_p^{left}}{I_p^{right} + I_p^{left}}, \quad CD_s = \frac{I_s^{right} - I_s^{left}}{I_s^{right} + I_s^{left}}, \qquad (1)$$

where I_i^j is the SHG intensity, the superscripts $j = right, left$ denote the polarization of the fundamental beam, and the subscripts $i = p, s$ denote the polarization of the second-order response.

Magnetization-induced chirality effect in SHG was studied by placing the sample in an in-plane DC magnetic field of about 2 kOe formed by permanent NdFeB magnets that were glued in the aluminum frame; the latter was fixed on the same holder as the sample. We studied the effect of the magnetic field of the two orientations with respect to the U-shaped nanostructures, that was parallel or perpendicular to the symmetry axis of the sample. This allowed us to keep the constant relative orientation of the in-plane magnetic field and the sample during the anisotropy measurements.

Azimuthal anisotropy of the SHG response was studied when measuring the SHG intensity as a function of the azimuthal angle of the sample ψ [see Fig. 1(b)] determined as an angle between the Y axis of the coordinate frame associated with the sample, (X, Y, Z), and the Y' axis of the laboratory one, (X', Y', Z'). In these measurements, the sample was placed on the rotating stage, so that the ψ angle was changed continuously in the interval $0 \div 360^\circ$.

In order to take account of the extrinsic chirality in second harmonic response, we measured the azimuthal dependencies of the CD_p and CD_s in the absence and in the presence of the DC magnetic field of different orientations and sign. To do so, the SHG azimuthal dependence for s- or p-polarized second harmonic was measured 5–10 times for the left and then for the right circular polarization of the fundamental radiation, then the $CD_{p,s}(\psi)$ dependencies were calculated according to (1) for every orientation of the applied magnetic field. This procedure allowed us to measure both the SHG anisotropy associated with the symmetry of a single U element and of the array of U nanostructures, and the magnetic field effect. In order to obtain the true CD effect in SHG and get rid of the extrinsic chirality, the obtained $CD_{p,s}(\psi)$ dependencies were integrated over all the azimuthal orientations of the sample thus giving the averaged values $\langle CD_p \rangle$, $\langle CD_s \rangle$, similarly to our previous work [25].

III. EXPERIMENTAL RESULTS

Figure 2 shows the azimuthal dependencies of the CD effect for the s and p SHG polarizations in the absence of the magnetic field, calculated from the experimental $I_i^j(\psi)$ dependencies. It can be seen that the absolute value of the SHG CD strongly depends on the azimuthal position of the sample, reaches 10–20% at approximately $\psi = \pi/8 + \pi n/4$, $n = 0, 1, 2 \ldots$. This azimuthal position corresponds to the case when the structure is the most "asymmetric" with respect to the plane of incidence so that extrinsic chirality is the strongest. The observed nearly fourfold symmetry of the SHG azimuthal dependence can be attributed both to crystalline Si(100) substrate and to the $4m$ symmetry of the rectangular array of U-shaped nanoelements. Angular shift on the CD_s and CD_p dependencies is typical to the SHG response and is due to the different phase relationships between $\hat{\chi}^{(2)}$ components that contribute to the SHG signal in each case [25]. Similar measurements performed for larger angle of incidence ($\theta = 40^\circ$) showed similar SHG CD behavior.

At the same time, both CD_s and CD_p averaged over the 2π azimuthal angle interval turn out to be zero within the

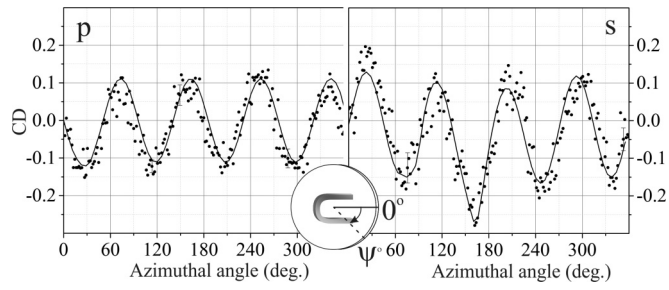

FIG. 2. Azimuthal dependencies of the circular dichroism of the s (right panel) and p (left panel) polarized SHG measured in the absence of the dc magnetic field, angle of incidence is $\theta = 20^\circ$. The orientation of the U-shaped nanoelement for the azimuthal position $\psi = 0^\circ$ is shown schematically in the inset. Solid line is the result of the approximation for the m-symmetric structure.

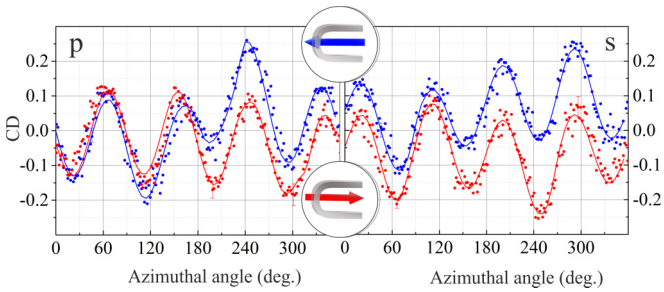

FIG. 3. Azimuthal dependencies of the circular dichroism of the s (right panel) and p (left panel) polarized SHG with applied magnetic field in the right (red dots) and left (blue dots) directions, angle of incidence $\theta = 20^\circ$.

experimental accuracy, which indicates that the underlying SHG CD mechanism is the extrinsic chirality of the SHG response of U-shaped achiral structure [23].

Figure 3 shows the results of analogous SHG CD measurements performed for the array of U-shaped nanostructures subjected to the dc magnetic field applied in the direction parallel to the mirror plane of the metasurface, as shown in the inset of Fig. 3. This orientation of the magnetic field was chosen in order to break the mirror symmetry of a single planar U-shaped element as well as of the array in a whole. The data obtained for the opposite directions of the magnetic field are shown in red and blue, correspondingly. In that case, similarly to the nonmagnetized sample, the SHG CD azimuthal dependence is anisotropic with expected dominant fourfold symmetry. At the same time, a distinct difference appears, namely, the average circular dichroism values are nonzero and are different in sign for the opposite orientations of the dc magnetic field: $\langle CD_p(+H)\rangle = (2 \pm 1)\%$, $\langle CD_s(+H)\rangle = (6 \pm 1)\%$ for the nominal positive magnetic field shown by blue arrow in the inset ($+H$, blue data), and $\langle CD_p(-H)\rangle = (-3 \pm 1)\%$, $\langle CD_s(-H)\rangle = (-7 \pm 1)\%$ for the magnetic field orientation shown by red arrow. Nonzero values of the $\langle CD_p\rangle$, $\langle CD_s\rangle$ indicate the appearance of true chirality in anisotropic magnetized metasurface composed of achiral nanoelements.

At the same time, as the magnetic field is oriented perpendicularly to the symmetry axis of the U-shaped element, the average values of the SHG CD are again close to zero for both SHG linear polarizations: $\langle CD_p\rangle = (1 \pm 1)\%$, $\langle CD_s\rangle = (0.6 \pm 1.0)\%$, which shows the absence of chirality of the structure in this case.

IV. DISCUSSION

The experiments described above show that in the presence of dc magnetic field of definite orientation with respect to anisotropic achiral metasurface composed of mirror-symmetric nanostructures can demonstrate circular dichroism effect distinct from extrinsic chirality. In other words, we show the effect of magnetization-induced chirality of magnetized achiral metasurface. The underlying mechanism is the following.

It is well known that magnetization breaks the time reversal symmetry of the structure. Our idea on magnetization-induced chirality was to reduce the symmetry of a mirror-symmetric structure by application of the magnetic field along the symmetry axis, which was done in the experiments illustrated by Fig. 3. We saw that while a strong SHG anisotropy in the SHG CD effect remains, still the averaged SHG CD value, $\langle CD_{p,s}\rangle$, is nonzero. In the absence of the magnetic field, the structure has the mirror symmetry plane (XOZ), thus the following nonzero components of $\hat{\chi}^{(2)}$ tensor describe the SHG response: χ_{xxx}, χ_{xyy}, $\chi_{yxy} = \chi_{yyx}$, χ_{xzz}, $\chi_{xxz} = \chi_{xzx}$, $\chi_{yyz} = \chi_{yzy}$, χ_{zxx}, χ_{zyy}, χ_{zzz}, $\chi_{zzx} = \chi_{zxz}$ [26]. It should be noted here that there are two sources of different symmetries that contribute to SHG in our samples, the first one being the m-symmetric array of U-shaped nanoelements, and the second one is the Si(100) surface with the 4m point symmetry group, while their contributions can't be distinguished. At the same time, all the $\hat{\chi}^{(2)}$ components that determine the SHG anisotropy are achiral, so after the averaging over the azimuthal angle (and thus eliminating the influence of anisotropy and leaving just purely chiral contribution) the SHG CD values are zero for both registered SHG polarizations (Fig. 3). Analogous results were obtained in gold nanowires [23] when varying the angle of incidence of the probe beam θ from positive to negative values, which is equivalent to the change of the azimuthal angle ψ to $\psi + \pi$ in our case.

The presence of magnetization oriented along the Ox axis breaks the time reversal symmetry [27–29] and odd-in-magnetization $\hat{\chi}^{(2)M}$ tensor components appear: $\chi^M_{xyz} = \chi^M_{xzy}$, $\chi^M_{yxz} = \chi^M_{yzx}$, $\chi^M_{zxy} = \chi^M_{zyx}$, $\chi^M_{xyx} = \chi^M_{xxy}$, $\chi^M_{zyz} = \chi^M_{zzy}$, χ^M_{yyy}, χ^M_{yxx}, χ^M_{yzz}, which change their sign under the inversion of the external magnetic field and are zero in the absence of magnetization. Importantly the first six $\hat{\chi}^{(2)M}$ components describe the chiroptical effects [30]. That is why the average values of the SHG CD from arrays of U-shaped nanoparticles are nonzero in the presence of magnetization. The sign of $\langle CD_p\rangle$ and $\langle CD_s\rangle$ is defined by chiral components of the $\hat{\chi}^{(2)M}$ tensor, which, in turn, depends on the direction of the magnetic field applied along the Ox axis. Thus the reversal of the magnetic field changes the sign of the average SHG CD value (Fig. 3). At the same time, the comparative analysis of the SHG CD azimuthal dependences for the p and s polarizations of second harmonic, i.e., the modulation depth and asymmetry of these curves, cannot be performed, as they are determined by all the chiral $\chi^{(2)}$ components mentioned above, each of them being a complex number.

Nonlinear-optical response of the U-shaped structures with the applied magnetic field of opposite directions is similar to that of chiral enantiomorphs [25]. That is why we can announce here the experimental observation of magnetization-induced chirality in the SHG response of symmetric nanostructures. It should be mentioned that the value of the $\langle CD_s\rangle$ reaching 6% is noticeable enough in comparison to that of the gold chiral-shaped G structures (maximum value 8%) studied in Ref. [25].

Zero values of the averaged SHG CD effect in the presence of the magnetic field applied in the plane of the sample and perpendicular to the U-shaped nanoelements are attained as in that case magnetization does not break the mirror symmetry of the structure. In that case no additional chiral $\hat{\chi}^{(2)M}$ tensor components appear, so the average SHG CD values are zero, although the dependencies $CD_p(\psi)$ and $CD_s(\psi)$

reveal nearly fourfold symmetry due to the anisotropy of the structure.

It should be also noted that the values of $\langle CD_p \rangle$ and $\langle CD_s \rangle$ in the presence of magnetization increase with decreasing of the angle of incidence. It occurs due to the amplification of the contribution of in-plane-magnetization-induced components of $\hat{\chi}^{(2)}$ tensor with θ decreasing as discussed in the paper [31].

V. CONCLUSION

In conclusion, we observe magnetization-induced circular dichroism effect in second harmonic generation in symmetric arrays of U-shaped permalloy nanoelements subjected to the dc magnetic field. Azimuthal dependencies of this effect averaged over the azimuthal orientations of the structure is shown to be zero in the absence of magnetization and reaches 6% under the application of the symmetry-breaking magnetic field. We show that the sign of averaged SHG CD can be controlled by the direction of magnetization.

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