Asymmetric second harmonic generation in chiral optical metamaterials

V. K. Valev[1,*], A. V. Silhanek[2], W. Gillijns[2], O. A. Aktsipetrov[3], V. V. Moshchalkov[2]
T. Verbiest[1]

[1] Molecular Electronics and Photonics, INPAC, Katholieke Universiteit Leuven, Celestijnenlaan 200 D, B-3001 Leuven, Belgium.
[2] Nanoscale Superconductivity and Magnetism, Pulsed Fields Group, INPAC, Katholieke Universiteit Leuven, Celestijnenlaan 200 D, B-3001 Leuven, Belgium.
[3]Department of Physics, Moscow State University, 11992 Moscow, Russia
*Corresponding author: v.k.valev@fys.kuleuven.be

ABSTRACT

We report that in the absence of electric dipole contributions, upon azimuthal sample rotation, the corresponding SHG response was found to be chiral, i.e. it shows the presence of asymmetries with a sense of rotation (lack of mirror symmetry). It was found that this sense of rotation reverses with the handedness configuration (G and mirror-G, see Fig. 1). While it is apparent that the property originates in local field enhancements of electric and/or magnetic multipoles, its explanation invites further theoretical research.

Keywords: Second Harmonic Generation, SHG, metamaterials, nanostructures, chirality, nanoscience, nonlinear optics, asymmetric second harmonic generation, ASHG

INTRODUCTION

Nanopatterned metal films have had an important impact on optical sciences, both with respect to fundamental phenomena and in terms of applications.[1,2,3] There is literally an infinite number of possible arrangements for the metallic nanostructures and, in conjunction with their unusual physical properties, this richness justifies their classification as a whole new type of materials – metamaterials. The prefix "meta" suggests that the properties of these materials somehow transcend those of "ordinary" matter.

Several definitions of metamaterials can be found currently. For instance, the term designates regular arrays of nanostructures with dimensions much smaller than the wavelength of the incident light. A metamaterial is also one in which the magnetic component of the electromagnetic radiation plays a significant role. A metamaterial is one with negative refractive index. So what is a metamaterial?

The most general definition is that a metamaterial is any artificial material fabricated to exhibit specific optical properties which are not readily available in nature. Several very appealing phenomena have been associated with metamaterials, such as invisibility,[4] negative refraction[5,6,7] or super-lensing.[8,9] Due to their spectacular nature, a large interest in studying optical fields at the nanoscale has arisen.

It has been established that surface and interface plasmon resonances play an important role in all these new effects. Plasmons are naturally occurring collective excitations of the electrons at the surface of a metal. On the surface of a homogenous thin metallic film, they are randomly distributed. However, a regular arrangement of nanostructures induces a periodicity, which can order and enhance the plasmons. The term "resonance" here designates a wavelength of light for which the optical response of the system is maximized. These electromagnetic field enhancements are very sensitive to the wavelength of the incident beam, and, to the immediate surroundings of the nanostructures. Additionally, the local fields can be further enlarged by the so called "electrostatic lightning rod effect". This phenomenon is encountered at geometric

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singularities or sharp curvatures, where the field lines become intensely crowded, similarly to what can be observed at the pointed extremity of a lightning rod.

Because the physical mechanisms responsible for the unusual properties of metamaterials originate in field enhancements at the surfaces of the nanostructures, their study would clearly benefit from surface specific probes. Furthermore, we can expect a dramatic impact on the response of surface specific optical techniques, such as, for instance, Second Harmonic Generation (SHG).

Within the dipole approximation, SHG is forbidden in centrosymmetric materials and consequently it appears only in regions of broken symmetry, namely surfaces and interfaces. The sensitivity of the techniques down to the atomic level is well established and henceforth it seems designated for investigating the surface field enhancements in metamaterials. And indeed, the nonlinear properties of nanomaterials have attracted an increasing amount of interest.[10,11,12,13,14,15]

Recently, chiral metamaterials have become the focus of great attentions since negative refractive index in this type of materials was predicted[16] and reported.[17,18] Chirality is a property that breaks the symmetry in centrosymmetric media and consequently SHG from chiral surfaces and interfaces is allowed. For instance, chiral symmetry breaking has been reported from small defects in nanoparticles[19,20,21,22] and from nanopatterned thin films.[23,24]

Of particular importance for this paper is the fact that, in the last few months, two novel ways to observe chirality in optical materials were demonstrated. While chirality in optics has traditionally been associated with *circularly* polarized light, both of these new properties involve *linearly* polarized light. First, it was shown that SHG microscopy images can reveal directly the handedness in G-shaped planner chiral nanostructures, made of gold.[25] And second, it was revealed that it is possible to distinguish the handedness in this chiral material by rotating the sample in a more traditional farther-field experiment.[26] This last property is rather counter-intuitive since chirality is generally invariant under rotational symmetry. More specifically, in Ref. 26 it was shown that, upon azimuthal sample rotation, the corresponding SHG response is chiral, i.e. it shows the presence of asymmetries with a sense of rotation (lack of mirror symmetry). This experiment was performed in a polarizer-analyzer configuration where the chiral electric dipole contribution was expected to be dominant. It was also demonstrated that chirality can be observed without electric dipole contribution but only as a difference of peak intensity between the SHG signals from both chiralities, i.e. in the absence of electric dipole contribution, no asymmetry in the SHG was reported.

Here we report that in the absence of electric dipole contributions, upon azimuthal sample rotation, the corresponding SHG response was found to be chiral, i.e. it shows the presence of asymmetries with a sense of rotation (lack of mirror symmetry). It was found that this sense of rotation reverses with the handedness configuration (G and mirror-G, see Fig. 1). While it is apparent that the property originates in local field enhancements of electric and/or magnetic multipoles, its explanation is not trivial.

THEORY

The second-harmonic response can be described by a nonlinear polarization, which is expressed in the electric-dipole approximation as:[27]

$$\mathbf{P}^{NL}(2\omega) = \chi^{(2)}\mathbf{E}(\omega)\mathbf{E}(\omega), \tag{1}$$

Where ω is the frequency of light, $\chi^{(2)}$ is the second order susceptibility tensor and $\mathbf{E}(\omega)$ the electric field component of the incident light. It follows from this formula that SHG can only be generated in noncentrosymmetric materials or regions of matter that lack inversion symmetry, such as surfaces and interfaces. Indeed, since upon applying an inversion symmetry (that where x, y and z transform into –x, -y and –z) the vector quantities $\mathbf{P}$ and $\mathbf{E}$ change sign and as a consequence $\mathbf{P}^{NL} = \chi^{(2)}\mathbf{E}(\omega)\mathbf{E}(\omega)$ transforms into $-\mathbf{P}^{NL} = \chi^{(2)}\left[-\mathbf{E}(\omega)\right]\left[-\mathbf{E}(\omega)\right]$. This can only be valid if the susceptibility is zero.

In noncentrosymmetric materials, $\chi^{(2)}$ is a third rank tensor with 27 components. However, depending on the symmetry of the material, the number of nonvanishing susceptibility components can be significantly reduced. For an in-plane isotropic chiral sample (C_∞ symmetry) the second order susceptibility becomes:

$$\chi^{(2)} = \begin{pmatrix} 0 & 0 & 0 & \chi_{xyz} & \chi_{xxz} & 0 \\ 0 & 0 & 0 & \chi_{yyz} & \chi_{yxz} & 0 \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & 0 & 0 & 0 \end{pmatrix}, \tag{2}$$

where $\chi_{xzz} = \chi_{yzz}$, $\chi_{xxz} = \chi_{yyz}$ and $\chi_{xyz} = -\chi_{yxz}$. This last component leads to the appearance of nonlinear optical activity (the nonlinear equivalent of optical activity). Often this component is referred to as the chiral one, since it is present only in chiral systems. The other components are referred to as achiral because they occur in both chiral and achiral systems.

It has been shown that the second-harmonic field can be conveniently written in terms of the S- and P-polarized components of the fundamental field:

$$I_{S,P}(2\omega) = \left| f_{S,P}\mathbf{E}_P^2(\omega) + g_{S,P}\mathbf{E}_S^2(\omega) + h_{S,P}\mathbf{E}_P(\omega)\mathbf{E}_S(\omega) \right|^2, \tag{3}$$

where the coefficients $f_{S,P}$, $g_{S,P}$ and $h_{S,P}$ are complex parameters, which are linear functions of the first order nonlinear susceptibility tensor elements. In the following, we shall indicate the real and imaginary part of these complex numbers by the indices "Re" and "Im", respectively. The exact form of these coefficients depends on the symmetry of the sample. Furthermore, they are different for the reflected and transmitted second harmonic light and they also depend on the angle of optical incidence.

Neglecting the refractive indices, for a chiral isotropic surface in the electric dipole approximation and in the reflection geometry, the dependence of $f_{S,P}$, $g_{S,P}$ and $h_{S,P}$ on the different susceptibility components takes the following form:[28]

$$\begin{aligned} f_S &= \sin\theta\left(2\chi_{xyz}\cos\theta\right) \\ g_S &= 0 \\ h_S &= \sin\theta\left(2\chi_{xxz}\right) \\ f_P &= \sin\theta\left(2\chi_{zzz}\sin^2\theta + \chi_{zxx}\cos^2\theta + 2\chi_{xxz}\cos^2\theta\right) \\ g_P &= \sin\theta\left(\chi_{zxx}\right) \\ h_P &= -\sin\theta\left(-2\chi_{xyz}\cos\theta\right) \end{aligned} \tag{4}$$

where the subscripts *S* and *P* refer to the particular component of the SH-field.

Plotting the SHG intensity as a function of wave-plate angle, allows one to extract the values of $f_{S,P}$, $g_{S,P}$ and $h_{S,P}$. For a wave-plate of retardation δ (where $\delta = \pi/2$ is a half wave-plate and $\delta = \pi/4$ is a quarter wave-plate), the fitting formula for the second harmonic intensity as function of the state of polarization of the incoming beam, which is determined by the initial state of linear polarization and the rotation of an angle θ_{WP} of the wave-plate, can be expressed by the following formulas.

For P-polarized light before the quarter wave-plate: [29]

$$
\begin{aligned}
I^{P-in}(2\omega) = \frac{1}{4}\Big[& -2f_{\mathrm{Re}}\cos^2\delta + (f_{\mathrm{Re}} + g_{\mathrm{Re}})\sin^2\delta + (f_{\mathrm{Re}} - g_{\mathrm{Re}})\sin^2\delta\cos 4\theta_{WP} \\
& - 2f_{\mathrm{Im}}\sin 2\delta\cos 2\theta_{WP} + h_{\mathrm{Re}}\sin^2\delta\sin(4\theta_{WP})\Big]^2 \\
& + \frac{1}{4}\Big[-2f_{\mathrm{Im}}\cos^2\delta + (f_{\mathrm{Im}} + g_{\mathrm{Im}})\sin^2\delta + (f_{\mathrm{Im}} - g_{\mathrm{Im}})\sin^2\delta\cos 4\theta_{WP} \\
& + 2f_{\mathrm{Re}}\sin 2\delta\cos 2\theta_{WP} + h_{\mathrm{Re}}\sin 2\delta\sin 2\theta_{WP}\Big]^2
\end{aligned}
\tag{5}
$$

And for S-polarized light before the wave-plate:

$$
\begin{aligned}
I^{S-in}(2\omega) = \frac{1}{4}\Big[& 2g_{\mathrm{Re}}\cos^2\delta - (f_{\mathrm{Re}} + g_{\mathrm{Re}})\sin^2\delta + (f_{\mathrm{Re}} - g_{\mathrm{Re}})\sin^2\delta\cos 4\theta_{WP} \\
& - g_{\mathrm{Im}}\,2\sin 2\delta\cos 2\theta_{WP} + h_{\mathrm{Re}}\sin^2\delta\sin(4\theta_{WP})\Big]^2 \\
& + \frac{1}{4}\Big[2g_{\mathrm{Im}}\cos^2\delta - (f_{\mathrm{Im}} + g_{\mathrm{Im}})\sin^2\delta + (f_{\mathrm{Im}} - g_{\mathrm{Im}})\sin^2\delta\cos 4\theta_{WP} \\
& + g_{\mathrm{Re}}\,2\sin 2\delta\cos 2\theta_{WP} - h_{\mathrm{Re}}\sin 2\delta\sin 2\theta_{WP}\Big]^2
\end{aligned}
\tag{6}
$$

In these equations, we have omitted the S and P indices for clarity of the notation.

It should be noted that Equations 5 and 6 describe correctly the SHG intensity not only in the electric dipole approximation but also in the case of higher order multipoles, such as, for instance, magnetic dipoles and electric quadrupoles. These quantities would then appear as additional terms in Equation 4.

EXPERIMENTS

SHG measurements were performed with a Mai-Tai femtosecond laser system at a wavelength of 800 nm. Figure 1 shows the essential features the experiment. The initial beam polarization was set by means of a Glan-Thompson polarizer. Subsequently, the rotation by an angle θ_{WP} of a quarter wave-plate modulated the polarization from left- to right-circularly polarized states. Next, the fundamental light, having a power of 300 mW, was focused on the sample through a lens of 10 cm focal length. The angle of optical incidence on the sample θ was 45°. The sample was mounted on a motorized rotation stage. After reflection, the second harmonic was filtered through a BG39 filter, while the 800 nm radiation was blocked. The beam then passed through an analyzer and reached a XP2020 photomultiplier tube. The electronic signal was then detected with a lock-in (Stanford Research SR830), triggered at 750 Hz by an optical chopper, which was placed between the polarizer and the wave-plate.

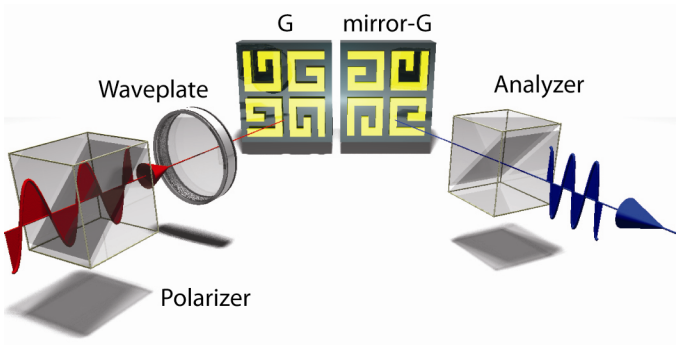

Fig.1. The structure of the G-shaped gold nanostructures.

The investigated samples consist of a periodic array of G-shape microstructures made of a Au(25 nm) film evaporated by DC sputtering system on top of a Si/SiO_2 substrate. For the sample preparation we first cover the substrate with a double polymethyl metacrylate-methyl metacrylate resist layer in which the array of G-shape structures is defined by electron-beam lithography. After the bilayer deposition, the resist is removed by a liftoff procedure. Figure 2 shows scanning electron microscopy images of the two chiral structures investigated. The lateral size of each individual motif is 1 μm wide, the line width is 200 nm and the separation between neighboring structures is 200 nm. The whole array covers an area of 2.5×2.5 mm^2.

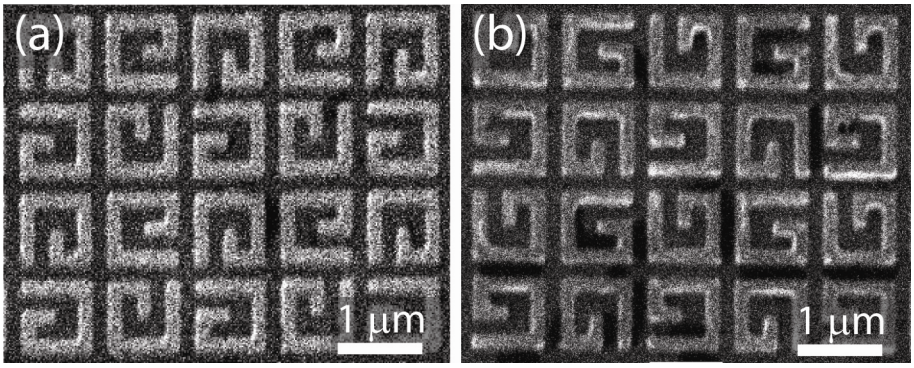

Fig.2. Scanning electron microscopy images of the samples with structures G, in (a), and mirror-G, in (b).

RESULTS

Typically, the SHG response in thin films is due to the broken material symmetry at the interfaces, where electric dipoles contributions dominate. Because our samples have a fourfold symmetry – see Fig. 2 – their nonlinear susceptibility response is described by the C4 symmetry group tensor, which is identical to the one in Equation 2. Fig. 3 shows the SHG intensity as a function of the azimuthal rotation angle of the sample for both chiralities, with both the polarizer and the analyzer along the vertical direction (i.e. S_{IN}-S_{OUT}). In this particular polarizer-analyzer configuration electric dipole contributions are forbidden, as it can be seen in Equation 4, where $g_S = 0$. Consequently, the SHG response in Fig. 3 can be attributed to higher order multipoles only, see Ref. 26 for a more detailed discussion of the origin of the signal in our samples.

The peaks in Fig. 3 cover a sample rotation range of 90°. Because of the fourfold symmetry of the samples, these data are representative of the complete 360° SHG response. Careful examination of the peaks in Fig. 3a and 3b clearly reveals the occurrence of asymmetries, which indicate a sense of rotation that is opposite for both samples. The arrows indicate the asymmetric features and it is clear that they reverse from the G sample to mirror-G.

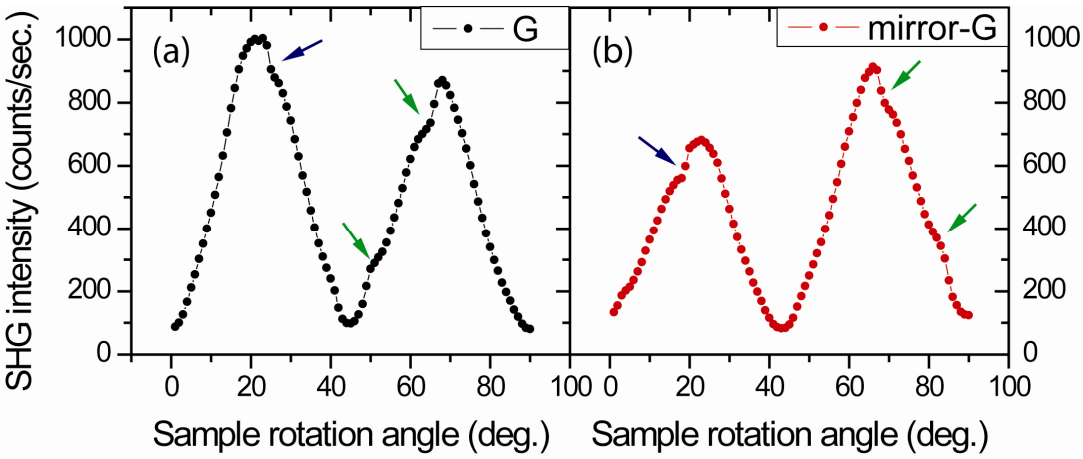

Fig.3. The SHG intensity as a function of the azimuthal rotation angle of the sample for both chiralities. Both the polarizer and the analyzer were oriented along the vertical direction. In (a) and (b), the two distinctive peaks are shown for the G and mirror-G structures, respectively.

According to equation 4, in the electric dipole approximation $g_S = 0$. Clearly, here this is not the case and attempting to fit the data with such constraints was found to be impossible. Consequently, based on this nonlinear optical experimental evidence, the role of higher order multipoles in the chirality of these samples was confirmed. Currently, attempts at fitting the data in order to reproduce the features highlighted by the arrows in Fig. 3 are being made. This task is rendered particularly challenging since both electric and magnetic multipoles should be taken into account.

CONCLUSION

We presented result showing that in the absence of electric dipole contributions, upon azimuthal sample rotation, the corresponding SHG response was found to be chiral, i.e. it showed the presence of asymmetries with a sense of rotation (lack of mirror symmetry). It was found that this sense of rotation reverses with the handedness configuration (G and mirror-G, see Fig. 1). While it is apparent that the asymmetry in SHG signal originates in local field enhancements of electric and/or magnetic multipoles, its explanation remains challenging.

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