Nonlinear Optics of Magnetic Crystals

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Nonlinear optics of magnetic crystals is a very recent field that exhibits a number of unusual optical phenomena. Using the electric dipole approximation we discuss the crystallographic and magnetization-induced nonlinear susceptibilities that coexist in magnetic crystals. It is the interference between the nonlinear optical waves of different origin that is the source of novel magneto-optical effects, such as transversal linear in M effect at normal incidence, circular dichroism with no equivalence between light helicity and magnetization direction change, etc., that have no equivalent in linear optics. As a model system for experimental studies we used thin epitaxial films of magnetic garnets grown on substrates with different crystallographic orientations. The second harmonic generation (SHG) was studied in the spectral range of 0.71-0.84 μm. These experiments were done in both transverse and longitudinal geometries. The experimental data on the SHG rotational anisotropy perfectly confirm the predicted effects.

Keywords: magneto-optics, optical second harmonic generation, magnetic garnets

1. Introduction

The field of nonlinear magneto-optics started only very recently by the prediction 1,3 of magnetization-induced changes of the SHG intensity from a magnetic samples. Surface and interface sensitivity of SHG from magnetic materials 4,5 appeared to be combined with huge magneto-optical effects 5. It appeared that not only the differences in the wave equations played a role, as pointed out by Pustogowa et al. 9, but also that the differences in the symmetry properties between the nonlinear and linear response tensors can lead to additional enhancements of several orders of magnitude. These strong, surface sensitive, nonlinear magnetooptical effects have already successfully been applied for the study of the magnetic properties of surfaces and ultra thin films.

So far, however, the crystallographic symmetry of magnetic samples was not seriously taken into account, except for a very few cases (see Refs. 10-12). There should be very interesting consequences of the interference between the nonlinear optical waves coming from the two sources of symmetry breakings: the space-inversion symmetry and that of time-reversal. As a result, the nonlinear magneto-optical effects become closely connected to the crystallographic structure. Also, new magneto-optical effects can appear that have no equivalence in linear optics.

The present paper reports a detailed study of nonlinear magneto-optical phenomena in magnetic crystals. The origin of these phenomena lies in the two sources of nonlinear polarization that may coexist in any magnetic crystal. The first one is due to the crystallographic contribution which arises in the electric-dipole approximation in non-centrosymmetric crystals. This contribution to SHG is rather well studied in many materials. The second one is of magnetic origin and was observed only recently. In this paper we study, both theoretically and experimentally, SHG in thin films of magnetic garnets. These are a well studied group of materials characterized by a large variety of magnetic, optical, and magneto-optical properties. Several experiments showed that SHG can be readily observed in magnetic garnet films 10,13,14. We analyse the symmetry properties of the two contributions to SHG from magnetic crystals of different symmetries and show how they can be unambiguously separated. It appears that the interference of these two contributions gives rise to several new optical phenomena that do not exist in linear (magneto-) optics. Special attention was paid to classify the phenomena as a function of the crystal symmetry.

2. Theory

An incident light wave induces a polarization in a medium that serves as a source for the transmitted and reflected light. This polarization P can be written in the electric dipole approximation as an expansion in powers of the electric field E(ω) of the incident wave:

$$P = \chi^{(1)}E(\omega) + \chi^{(2)}E(\omega)E(\omega) + \ldots$$  \hspace{1cm} (1)

The tensor \(\chi^{(1)}\) is the linear optical susceptibility. SHG is described by the second term, with the corresponding nonlinear tensor \(\chi^{(2)}\). In the presence of a magnetization, \(\chi^{(2)}\) should be further expanded in powers of M:

$$\chi^{(2)} = \chi_0^{(2)} + \frac{\partial \chi^{(2)}}{\partial M} M + \ldots$$  \hspace{1cm} (2)

Once can think about the first term as describing purely crystallographic effects while the second one only exists in the presence of a magnetization. Hence the total nonlinear optical polarization of a medium (in the electric dipole approximation) can be written as:
\[ P_1(2\omega) = P_1^{(cr)}(2\omega) + P_1^{(magn)}(2\omega) = \chi_{13}^{(2)} E_1(\omega)E_3(\omega) + \chi_{13}^{(3)} E_1(\omega)E_3(\omega)M_1(0) \]  

(3)

where \( P^{(cr)} \) and \( P^{(magn)} \) are the crystallographic and magnetic contributions, respectively. \( E(\omega) \) is the fundamental optical field and \( M(0) \) is a spontaneous or magnetic-field-induced static magnetization. Both the \( P^{(cr)} \) and \( P^{(magn)} \) contributions are of the electric-dipole character, because they are proportional only to \( E(\omega) \). They are simultaneously allowed in non-centrosymmetric media, but their properties are different:

(i) \( P^{(cr)} \) is described by a polar tensor \( \chi_{13}^{(2)} \) of rank 3, whereas \( P^{(magn)} \) is described by an axial tensor \( \chi_{13}^{(3)} \) of rank 4. They exhibit a characteristically different rotational anisotropy that may strongly depend on the magnetization orientation in the crystal, similarly as was predicted for magnetized surfaces. 10

(ii) In nonabsorbing materials \( \chi_{13}^{(2)} \) is a real but \( \chi_{13}^{(3)} \) is an imaginary tensor 11,15. The corresponding nonlinear waves have a 90° phase shift and thus cannot interfere. However, interference becomes allowed when one or both of them are complex. This interference is very essential for the appearance of the nonlinear magneto-optical effects.

(iii) The two contributions to \( P(2\omega) \) should vary differently as a function of temperature. \( P^{(cr)} \) probes the degree of a crystal lattice non-centrosymmetry. It may depict anomalies at structural phase transitions. \( P^{(magn)} \) should reflect a temperature variation of the magnetization and thus vanishes at the transition from a magnetically ordered to a paramagnetic state.

To obtain a \( P^{(cr)} \neq 0 \) for normal incidence the in-plane symmetry must be rather low 10, while for the interference, a simultaneous existence of a nonzero \( P^{(magn)} \) is necessary.

3. Experimental details

3.1. Samples

Crystallographic, magnetic, optical, and magnetooptical properties of bulk crystals and thin films of magnetic garnets are thoroughly discussed in several books and review papers, see e.g. Ref. 10. Bulk crystals of magnetic garnets like the best known yttrium iron garnet \( Y_3Fe_5O_{12} \), belong to the cubic centrosymmetric space group \( Ia3d \ (O_\text{h}^{10}) \). Consequently, SHG in garnets is forbidden in the electric dipole approximation and we are unaware of any experimental reports concerning the observation of SHG in bulk garnet crystals.

The ferrimagnetic structure of \( Y_3Fe_5O_{12} \) is formed by two oppositely oriented magnetic sublattices, octahedral and tetrahedral ones. This type of magnetic ordering does not destroy the inversion center of the magnetic unit cell and thus cannot induce a bulk SHG of the electric-dipole type. To prove this independently we studied SHG in thin platelets cut from bulk crystals of yttrium gallium garnet \( Y_3Fe_5Ga_3O_{12} \ (x = 0.7) \). The SHG signals in these samples were several orders of magnitude lower than the SHG signals from thin films, and, in fact, could be related only to surface contributions.

In contrast to bulk crystals, thin epitaxial films of magnetic garnets are characterized by a non-cubic magnetic anisotropy. Films are grown on substrates cut from bulk cubic crystals of gadolinium gallium garnet \( Gd_3Ga_5O_{12} \) (GGG) or substituted GGG with a different lattice parameter. A uniaxial magnetic anisotropy in thin films is readily observed on (111)-type substrates as well as on the substrates of other orientations. Several models were proposed to explain the origin of the growth-induced non-cubic anisotropy that basically is related to the ordering of ions on the different crystallographic sites in the unit cell (it contains eight formula units) during the growth process of the film. Though deviations of the crystal symmetry from cubic in thin films are easily detectable by magnetic or optical birefringence measurements, in fact they have not been confirmed by X-ray diffraction techniques because of insufficient accuracy.

Moreover, the observation of the linear magnetooptical effect in thin films of magnetic garnets 17 proves that, in addition to the non-cubic distortion of the crystal structure, the center of inversion is lacking. This point is not important in the analysis of the magnetic structure and anisotropy of the films, but it plays a dominating role for the linear and especially nonlinear optical properties of the garnet films. For example, it allows the crystallographic SHG in the electric dipole approximation 10. The existence of the magnetic contribution to SHG in garnet films was demonstrated only recently 12.

The magnetic films used in the present study were grown by a liquid phase epitaxial method. Thin wafers of GGG and substituted GGG with a larger lattice parameter, with orientations (001), (110), (111), and (210) have been used as substrates. Samples differed in their compositions and lattice parameters. In total, more than 20 different samples were studied. The largest mismatch between lattice parameters of film and substrate was in the case of the (210) film, and the smallest one in the (110) film. In the (111) film the mismatch was negative.

Being such a modular system, thin films of magnetic garnets are ideal crystals to study nonlinear magnetooptics.

3.2 Method and experimental geometries

Plane-parallel samples were placed on a rotatable sample holder attached to a stepping motor. Most of the experiments were done in transmission at normal incidence with a laser beam propagating along the Z-axis (see Fig. 1). Rotating the sample by 360° around the Z-axis the SHG signal could be registered as a function of the azimuthal angle \( \varphi \). In the absence of a magnetic field these measurements provide the rotational anisotropy of the SHG signal due to the crystallographic contributions,
4. Results: nonlinear magneto-optical effects

4.1.1 Transversal effects: linear in M

The experimental results for this geometry showed that there is new nonlinear magneto-optical effect which is linear in magnetization $\mathbf{M}^2$. Note, in this transversal geometry only effects that are $\propto \mathbf{M}^2$ can be observed in the linear case, like magnetic linear birefringence. Such a novel nonlinear magneto-optical effect is a direct consequence of the interference between $\mathbf{P}^\text{cr}$ and $\mathbf{P}^\text{magn}$; without it, only $\propto \mathbf{M}^2$ effects can be found also in SHG (see the next section).

Fig. 2 shows the rotational anisotropy pattern for the (210) oriented film that clearly possesses the crystal symmetry $m$. For this symmetry, there are nonzero magnetic contributions for all four polarization combinations $\mathbf{M}$.

Experimentally, we do observe very strong SHG changes due to the magnetization reversal.

(110) films are worth to discuss separately. They have point group symmetry $mm2$ and the crystallographic contribution to SHG is not allowed at normal incidence. Nevertheless the experimental data for the (110) film showed a presence of SHG and therefore an interference is possible. This interference allows to distinguish $+\mathbf{M}$ and $-\mathbf{M}$ states. We found that the SHG rotational anisotropy for the (110) films can be well described by the same equations as for the crystal point group symmetry, either $m$ or $l$, though the rotational patterns of these types of films look differently (Fig. 3).

4.1.2 Transversal effects $\propto \mathbf{M}^2$

For (001)-oriented films, the situation is different. Here, the point group symmetry is $4mm$ leading to $\mathbf{P}^\text{cr} = 0$ for normal incidence. This means that here we expect a purely magnetization-induced SHG, and the SHG intensity should not be sensitive to the magnetization reversal in (001) films.

As mentioned before, in the (001) film no SHG signal was detected in the absence of a magnetic field. However, as predicted, in a magnetized sample an SHG signal was
observed, which was quadratic in $M$ and thus insensitive to the sign of the applied magnetic field. Thus, an SHG response can be "turned on" with the help of a magnetic field!

This is not only true for the film of this symmetry; in the (111) film clearly an isotropic addition to the SHG rotational anisotropy pattern appears, i.e. the SHG is also "turned on" with the help of a field for some particular crystallographic directions.

4.2. Magnetic effects: longitudinal configuration

In the longitudinal geometry, there is always a strong influence of the linear magneto-optical Faraday effect, which leads to the rotation of the light polarization due to a magnetization. Here, we will avoid the detailed discussion of the influence of these effects (see Ref. 19) for it by taking into account the polarization rotation at the fundamental frequency (which is easy to measure) and neglecting the same effect at the double frequency (because of the very short SHG light escape depth). Again, it is the interference of crystallographic and magnetic parts which leads to the linear in $M$ effects.

4.2.1 Nonlinear Faraday rotation

In the (111) films, in the longitudinal geometry Eq. 3 leads to the following rotational anisotropy of the SHG intensity:

$$I_{\text{SHG}}^{2\pi}(\pm M_z) \propto E_\| \cdot A \cdot 3\phi \pm BM_{\|} \sin 3\phi$$

Such an interference of the magnetic and crystallographic contributions leads to the rotation of the whole six-fold pattern for both polarization combinations. From the experimentally observed net rotation (see Fig. 4) we should subtract the Faraday rotation values for both the fundamental and second harmonic light.

Thus, this effect is very similar to the linear Faraday effect. The value of such nonlinear Faraday rotation angle can be easily calculated to be equal to:

$$\alpha_{NF} = -\arctan \left( \frac{BM_{\|}}{A} \right) = -\frac{BM_{\|}}{A} + ...$$

and this rotation is basically linear in the magnetization.

The rotation in (210) films is very similar; however a completely new effect appears which is discussed in the following section.

4.2.2 Nonlinear magnetic birefringence

Fig. 5 clearly shows a nonlinear magnetooptical effect that has no analog in linear optics. Indeed, the SHG intensity is changed (for some given crystal axes orientations) as a function of the magnetization reversal. This is actually an equivalent of the linear (speaking of the light polarization) magnetic birefringence which is however linear in magnetization and observed in the longitudinal geometry.

4.2.3 Nonlinear magnetic circular dichroism

It is well known that in linear optics there is a strict equivalence between the magnetization reversal and the change of the light helicity from left- to right-handed. This equivalence is due to the fundamental Onsager principle of the symmetry of the kinetic coefficients in the presence of...
a magnetic field or spontaneous magnetization. In the case of nonlinear magnetic circular dichroism (MCD) this equivalence breaks down, and the magnetization reversal is not equivalent to the change of the incoming light helicity. This is again very unusual from the point of view of linear magneto-optics. The inequivalence arises due to the interference of both time-invariant (crystallographic) and time-dependent (magnetic) contributions to the nonlinear MCD. Of course, this effect also depends on the sample symmetry.

For the nonlinear MCD measurements, the rotational anisotropy patterns were recorded for two opposite magnetization directions (±$M_Z$) fixed by the applied magnetic field. The value of the nonlinear $\delta_M$ was defined by the formula

$$
\delta_M = \frac{I^{2\omega}(+M_Z) - I^{2\omega}(-M_Z)}{I^{2\omega}(+M_Z) + I^{2\omega}(-M_Z)}
$$

(6)

for each fundamental light helicity. The results for the film of symmetry $m$ are shown in Fig. 6 (top panel). Clearly, the change of the light helicity reverses the sign of $\delta_M$, similar to MCD in linear optics.

The same result is also obtained for the $3m$-symmetry film. In contrast, in sample with crystal symmetry $l$, this statement is not true any more. It happens, that the values of $\delta_M$ for two different incoming light helicities (see Fig. 6 (bottom panel) and the inset) can be even of the same sign! Thus the strict equivalence between the magnetization reversal and the light helicity change is broken for the nonlinear MCD. The reason for this is again the interference between magnetic and crystallographic components of $\chi^{(2)}$, which makes the nonlinear magneto-optical effects to be directly dependent on the crystal structure.

5. Conclusions

The main result of this work is a comprehensive classification, both theoretically and experimentally, of the magneto-optical effects in SHG, as a function of the crystal structure. We have shown that a simultaneous breaking of space and time-reversal symmetry leads to a coexistence of two electric-dipole contributions to the nonlinear optical susceptibility: a crystallographic and a magnetic one. Such a coexistence can occur only in noncentrosymmetric media in an applied magnetic field or possessing magnetic ordering.

The unambiguous separation of the crystallographic and magnetic contributions to the net SHG signal is demonstrated with the help of rotational anisotropy experiments in an applied magnetic field, and at room temperature they were found to be of the same order of magnitude. The experimental data on the SHG rotational anisotropy perfectly confirm the predicted effects, such as transversal linear in $M$ effect at normal incidence, circular magnetic dichroism with no equivalence between light helicity and magnetization direction change, dichroism for linearly polarized light in longitudinal geometry, etc. The essential difference between the linear and nonlinear magneto-optical effects is that the latter ones are anisotropic. In the linear case, such an anisotropy may appear as a small correction only.
 Though we are able to explain the experimental data applying a simple symmetry analysis, a more profound microscopic theory is required to explain the absolute and relative values of the crystallographic and magnetization-induced nonlinear susceptibilities $\chi_{ijk}^{(2)}$ and $\chi_{ijk}^{(3)}$. In fact these two types of nonlinear susceptibility should also coexist in noncentrosymmetric molecules. However to study time-noninvariant contributions to the nonlinear magneto-optical response, magnetically ordered materials are most suitable because of their large values of the exchange splitting of the electronic states.

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