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Second harmonic generation spectroscopy in magnetic and multiferroic materials

R.V. Pisarev *

Ioffe Physical-Technical Institute, Russian Academy of Sciences, 26 Politekhnicheskaya Str., 194021 St. Petersburg, Russia

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ABSTRACT

Spectroscopic studies of magnetically ordered materials, multiferroic insulators, and magnetic semiconductors reveal several previously unexplored mechanisms of optical second harmonic generation (SHG). In contrast to non-magnetic materials, SHG in such systems is determined by arrangements of both charges and spins. In general, the nonlinear optical susceptibility arises from electric-dipole contributions in the case of noncentrosymmetric crystal structures and from magnetic-dipole contributions in the case of centrosymmetric crystal structures. We show that both these mechanisms are efficient in magnetic materials. Obeying different selections rules, SHG spectroscopy may provide new information in comparison to linear optics. The observation of resonance SHG at d–d transitions in antiferromagnetic oxides Cr_2O_3, NiO, CuB_2O_4 is discussed. The SHG spectroscopy was successfully applied for distinguishing subtle variations of magnetic structures in hexagonal manganites $RMnO_3$. Giant SHG in the region of charge-transfer transitions was observed in multiferroic manganite $TbMn_2O_5$. Spin-induced SHG was observed near the band gap in centrosymmetric magnetic semiconductors EuTe and EuSe. One of the most striking potentials of SHG is visualization of antiferromagnetic 180° domain structures which are indistinguishable in linear optics.

1. Introduction

SHG as the lowest-order nonlinear process plays a particular role in the vast field of nonlinear optics [1–4]. Simple symmetry considerations show that SHG in the leading electric-dipole (ED) order is only allowed in noncentrosymmetric materials. Therefore, in the past great experimental efforts have been invested into the search for new materials with large optical nonlinearities. Another benefit of SHG is its high sensitivity to surface and interface states of films and composite materials which is a consequence of the breaking of centrosymmetry at the boundary of otherwise centrosymmetric media.

Similar to breaking of space-inversion symmetry the breaking of time-inversion symmetry can lead to new contributions to SHG. Time-reversal symmetry is broken by long-range magnetic ordering or by applied magnetic field, so that new SHG contributions are induced and can be used as a probe for the magnetic structure and as supplementary tool for probing electronic structures. As early as in the 1960s and later nonlinear optical phenomena related to magnetic fields, magnetic ordering, and spontaneous magnetization were analyzed in several theoretical works [5–12].

Several attempts of experimental investigation of SHG induced by magnetic ordering were done [13–15], however a real experimental breakthrough occurred when a change of the SHG intensity from a ferromagnetic iron surface was observed upon reversal of magnetization by an applied magnetic field [16,17]. Evidence for an antiferromagnetic contribution to SHG was unambiguously proved in the study of magnetoelectric Cr_2O_3 [18]. Subsequently to this breakthrough, SHG in magnetically ordered substances became a subject of intensive experimental and theoretical research which is discussed in several review papers [19–22].

In contrast to SHG studies of metallic magnetic films where experiments are usually done at selected photon frequencies and no spectroscopic information is available [19,21], the main emphasis of the experiments discussed in this brief review is placed on *spectroscopic* studies of SHG in several classes of magnetically ordered dielectrics and semiconductors. We argue that only spectroscopic approach opens possibilities for distinguishing microscopical mechanisms of observed SHG.

2. Phenomenology of SHG in magnetic and multiferroic materials

For magnetically ordered materials the relation between the electric field components $\mathbf{E}(\omega)$ and $\mathbf{E}(\omega)$ of the fundamental light and the induced nonlinear polarization $\mathbf{P}(2\omega)$ in the ED

* Tel.: +7 812 2927963.
E-mail address: pisarev@mail.ioffe.ru

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approximation is given as

$$\mathbf{P}(2\omega) = \varepsilon_0(\boldsymbol{\chi}^{(i)} + \boldsymbol{\chi}^{(c)}) : \mathbf{E}(\omega)\mathbf{E}(\omega), \quad (1)$$

where the *time-invariant* (*i*-type) tensor $\boldsymbol{\chi}^{(i)}$ and the *time-noninvariant* (*c*-type) tensor $\boldsymbol{\chi}^{(c)}$ are responsible for crystallographic and linear spin-dependent contributions to the nonlinear polarization, respectively. The tensor components of $\boldsymbol{\chi}^{(i)}$ and $\boldsymbol{\chi}^{(c)}$ are uniquely defined by the crystallographic and magnetic structure of the crystal. Both types of tensors are tabulated in the Birss's monograph [23]. Neglecting dissipation, $\boldsymbol{\chi}^{(i)}$ is a real tensor while $\boldsymbol{\chi}^{(c)}$ is an imaginary tensor [5,12]. In the presence of absorption both tensors are complex, thus allowing interference of the form:

$$I(2\omega) \propto (|\chi^{(i)}|^2 + |\chi^{(c)}|^2 \pm 2|\chi^{(i)}||\chi^{(c)}| \cos\varphi)E^4(\omega), \quad (2)$$

with φ as the phase between *i*- and *c*-type susceptibilities. When the spin direction is reversed, φ changes by 180°, and the sign of the interference term $2|\chi^{(i)}||\chi^{(c)}| \cos\varphi$ is reversed so that the $\pm$ sign in Eq. (2) distinguishes opposite 180° domains. Note that the interference of crystallographic and magnetic contributions to SHG conserves both amplitude and phase of the involved light fields which will allow us to detect subtle nuances of magnetic structure such as the distribution of opposite 180° antiferromagnetic domains discussed in Section 6 [24].

In the case of multiferroic materials the coupling of the SHG process to ferroelectric or/and magnetic long-range order is expressed by the expansion:

$$\boldsymbol{\chi}^{(i)} = \boldsymbol{\chi}(0) + \boldsymbol{\alpha} : \mathbf{P}_S + \mathcal{O}[\mathbf{P}_S^2],$$

$$\boldsymbol{\chi}^{(c)} = \boldsymbol{\beta} : \mathbf{F}_M + \gamma : \mathbf{P}_S\mathbf{F}_M + \mathcal{O}[(\mathbf{P}_S, \mathbf{F}_M)^2]. \quad (3)$$

$\mathbf{P}_S$ is a polar vector describing pyroelectric polarization, and $\mathbf{F}_M$ is an axial vector in the case of ferro- or ferrimagnetically ordered crystals or a tensors of rank 1–3 in the case of antiferromagnetically ordered crystals. In the case of ferro- or ferrimagnetic order the term $\boldsymbol{\beta} : \mathbf{F}_M$ is often called magnetization-induced contribution.

The leading-order contribution to SHG is described as an ED transition, which is only allowed in noncentrosymmetric media. In contrast, the axial nature of magnetic field breaks time-inversion symmetry and should lead to new magnetic-field-induced second harmonic contributions allowing one to probe the *spin* (in contrast to the *charge*) of the electron. Similar to Eq. (3) one can write the coupling of SHG to static external electric fields $\mathbf{E}(0)$ or/and magnetic fields $\mathbf{H}(0)$ as:

$$\boldsymbol{\chi}^{(i)} = \boldsymbol{\eta} : \mathbf{E}(0) + \boldsymbol{\nu} : \mathbf{H}(0)\mathbf{F}_M + \mathcal{O}[(\mathbf{E}(0), \mathbf{H}(0))^2];$$

$$\boldsymbol{\chi}^{(c)} = \boldsymbol{\sigma} : \mathbf{H}(0) + \varsigma : \mathbf{E}(0)\mathbf{H}(0) + \boldsymbol{\tau} : \mathbf{H}(0)\mathbf{P}_S + \upsilon : \mathbf{E}(0)\mathbf{F}_M + \mathcal{O}[(\mathbf{E}(0), \mathbf{H}(0))^2] \quad (4)$$

Terms $\boldsymbol{\eta} : \mathbf{E}(0)$ and $\boldsymbol{\sigma} : \mathbf{H}(0)$ describe the electric field induced SHG and magnetic field induced SHG, respectively. The cross terms $\boldsymbol{\nu} : \mathbf{H}(0)\mathbf{F}_M$, $\varsigma : \mathbf{E}(0)\mathbf{H}(0)$, $\boldsymbol{\tau} : \mathbf{H}(0)\mathbf{P}_S$, and $\upsilon : \mathbf{E}(0)\mathbf{F}_M$ in Eqs. (3) and (4) describe more complex contributions.

3. SHG in antiferromagnetic crystals

3.1. Magnetoelectric Cr_2O_3

Cr_2O_3 crystallizes in the centrosymmetric point group $\bar{3}$m in which ED-SHG is forbidden. Below $T_N = 307.6$ K, the magnetic point group is $\bar{3}$m. In zero magnetic field the four Cr^{3+} spins are aligned along the rhombohedral optical axis in an alternating sequence of up and down spins which results in a noncentrosymmetric antiferromagnetic structure. Both space- and time-reversal symmetry operations are simultaneously broken, but the combined space-time-reversal operation $\bar{1}$ remains a symmetry element. With $\bar{3}$m as magnetic symmetry, axial *i*-tensors and polar *c*-tensors of odd rank are allowed in Cr_2O_3 [23]. One therefore may expect an MD contribution $\chi^{(i)}_{ijk}$ to SHG which is present above and below T_N, and further an ED contribution $\chi^{(c)}_{ijk}$ which is only present below T_N.

First observation of antiferromagnetic SHG was reported in Cr_2O_3 [18]. Fig. 1 shows the SHG spectra at 8 K in the region of the spin-forbidden $^4A_2 \rightarrow {}^2E, {}^2T_1$ transitions which correspond to the *R*-lines in ruby. Absorption spectra of these lines has been studied in detail [25–27]. In linear absorption spectrum the intensity of lines 1–5 is of the same order of magnitude. By contrast the feature 1 at 1.704 eV, which is a zero phonon line, reveals a SHG intensity which is 2–3 orders of magnitude higher than for the other lines. The 1.704 eV line has a spectral width of only 40 μeV

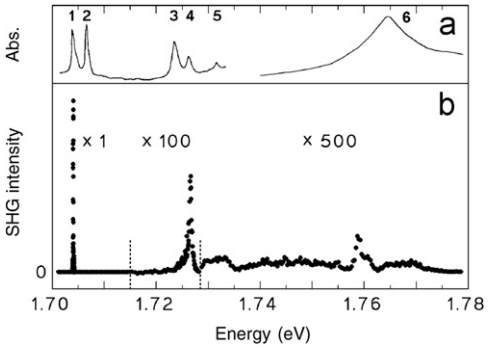

Fig. 1. (a) Schematic absorption spectrum [25–27] and (b) SHG spectrum of Cr_2O_3 in the region of the spin forbidden $^4A_1 \rightarrow {}^2E$, $^2T_1$ transitions [18].

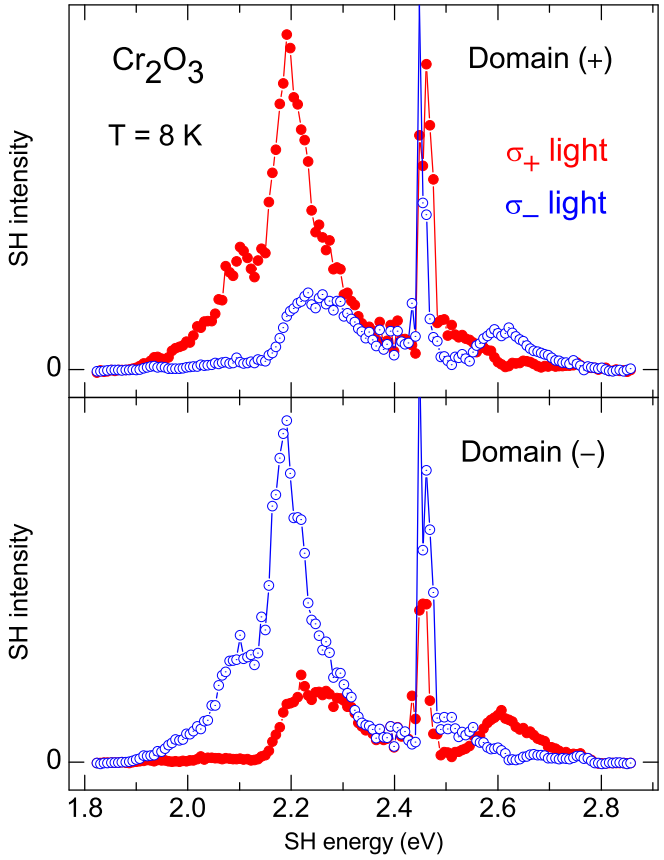

Fig. 2. SHG spectra of Cr_2O_3 in the region of a broad spin allowed transition $^4A_2 \rightarrow {}^4T_1$ and narrow spin-forbidden transition $^4A_2 \rightarrow {}^4T_2$ which depicts different response to $\pm$ circular polarizations of the incoming light [18]. For opposite antiferromagnetic domains $\pm$ circular polarizations are interchanged.