Time-reversal symmetry in nonlinear optics

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The applicability of time-reversal symmetry to nonlinear optics is discussed, both from macroscopic (Maxwell equations) and microscopic (quantum theoretical) point of view. We find that only spatial operations can be applied for the symmetry classification of nonlinear optical processes in magnetic, in particular antiferromagnetic, materials. An example is given where both operations (time reversal and a spatial operation) can yield different results.

Symmetries determine several important properties of a crystal, in particular, its optical response. In magnetic materials, time reversal is believed to be of fundamental importance since this operation reverses all magnetic moments.[1–3] However, the consequences of applying time reversal are more profound than a simple inversion of localized magnetic moments. As it will turn out in this paper there is a deep interrelation between the absence of conventional dissipation in even-order (e.g., second) harmonic generation and the influence of time reversal on spin ordering. This brings about a subtle difference between time-reversal and spatial symmetries in nonlinear optics. The benefit of this difference makes optical second harmonic generation (SHG) a rather unique probe of antiferromagnetism, while linear optics (where dissipation in the conventional sense is possible) is blind for such balanced spin structures. The recent discussion about the influence of microirreversibility on macroreversibility and reciprocity[4–6] shows that the issue of time reversal, although extensively discussed, is far from being understood.

The theory of nonlinear optics has been developed since the 1960s. The pioneering work of Armstrong *et al.*[7] describes the propagation of a light wave through a nonlinear medium, where the energy may be converted from the fundamental frequency to higher harmonics (or vice versa). An exhaustive description of nonlinear optical phenomena is contained in the fundamental books by Bloembergen[8] and Shen.[9] In these works,[7–9] a unique flow of time is tacitly assumed, while *magnetism* is entirely absent. Consequently the issue of time reversal is not essential for these authors. The discussion of magnetism has been brought to nonlinear optics by Pan *et al.*[10] and Hübner *et al.*[11] In these papers, time reversal was applied to reverse the localized magnetic moments, since the discussion was focused on ferromagnetism. However, the experimental observation of antiferromagnetic (AF) domains in Cr_2O_3 by Fiebig *et al.*[12] and the subsequent theoretical analyses by Muthukumar *et al.*[13] and by Dähn *et al.*[14] challenged the validity of time reversal for the symmetry analysis of optical processes. Since the inclusion or absence of time reversal in the theoretical analysis of SHG from antiferromagnets yields different predictions of the experimental results, the issue is shifted from academic interest to practical relevance. The importance of the theoretical analysis of SHG from antiferromagnets is tremendously growing due to the unique capabilities of this method in probing buried AF layers, which in turn is important for the characterization of recently upcoming magnetoelectronic devices such as tunneling magnetoresistive junctions.

In considering the time reversibility of an experimental situation, three approaches are possible: (i) time reversal is applied to the sample, but all the processes resulting from the experiment are unchanged. In particular, the magnetic moments in the sample are reversed, but the direction of the light propagation through the sample is not affected. This approach is presented, e.g., in Refs. 15 and 16. We consider this approach as incomplete, since it does not equally treat the sample and the light propagating through it. (ii) The second approach, usually encountered in the so-called Sagnac interferometry, addresses time reversal by reversing the propagation of the light through the sample (see, e.g., Refs. 17–19). Clearly, such procedure probes the *reciprocity* of the sample rather than its time-reversal symmetry. It can also be proven that the second approach is equivalent to the first one. (iii) According to the third approach, presented, e.g., in Ref. 20, time reversal acts on *both*: the sample and the experimental setup. In this paper, we will follow approach (iii).

In the processes of even-order harmonic generation, dissipation in the conventional sense, converting radiation into heat, does not exist, since the energy loss of the electromagnetic field is the time average[21]

$$-\left\langle \frac{dP(t)}{dt} E(t) \right\rangle, \tag{1}$$

which vanishes for SHG (and all even-order harmonics), since

$$P(t) \sim P_0 e^{i\omega t},$$

$$E(t) \sim E_0 e^{i2\omega t}. \tag{2}$$

Here, P and E denote the polarization of the medium and the electric field, respectively.[22] The lack of dissipation in the conventional sense does not mean that the process of SHG is reversible. Already the analysis by Armstrong *et al.*[7] assumes a unique time direction. There, the nonlinear polarization $\mathbf{P}^{NL}$ and the electric field $\mathbf{E}_3$ of a light beam resulting from Sum Frequency Generation at a point r_0 is given by

$$\mathbf{P}^{NL}(\omega_3) \sim \frac{1}{2}\mathrm{Re}[e^{i(\Delta\mathbf{k}\cdot\mathbf{r}_0+\Delta\phi)} e^{i(\mathbf{k}_3\mathbf{r}_0-\omega_3 t+\phi_3)}], \tag{3}$$

$$\mathbf{E}_3 \sim \mathrm{Re}[e^{i(\mathbf{k}_3\cdot\mathbf{r}_0-\omega_3 t+\phi_3)}]; \tag{4}$$

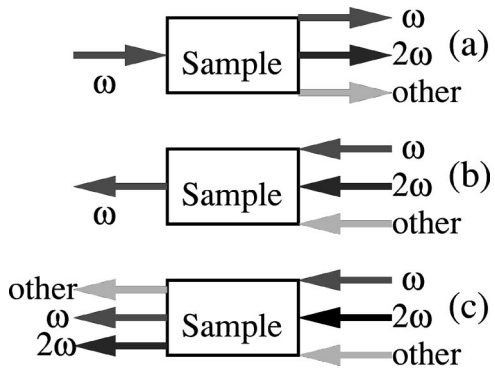

FIG. 1. Time-reversal asymmetry in SHG. Panel (a) presents the original process, panel (b) a process in reversed time which would restore the symmetry, panel (c) presents a physically valid process described in reversed time.

see Eqs. (3.1) and (3.2) of Ref. 7. Here, ω_3 and k_3 describe the frequency and wave vector of the generated light ($\omega_3 = \omega_1 + \omega_2$ and $\mathbf{k_3} \approx \mathbf{k_1} + \mathbf{k_2}$). The authors introduce the idea of ''work done on this wave'' by the nonlinear polarization of the medium, equal to

$$W_3 = \frac{\omega_3}{2\pi} \int_{cycle} \mathbf{E}_3 \frac{d\mathbf{P}^{NL}(\omega_3)}{dt} dt$$

$$= \frac{1}{2} \omega_3 \mathbf{E}_3 \mathbf{P}^{NL}(\omega_3, \text{ out of phase}), \tag{5}$$

if the polarization is exactly 90° out of phase with the electric field (which requires that $\Delta k_z z + \Delta\phi = \pi/2$). The work done on the generated wave *determines the direction of time*. This presents a new kind of dissipation, namely ''dissipation in the frequency space,'' which invalidates time-reversal symmetry.

This fact becomes even more obvious if one takes the global picture of SHG. Radiation acting on an *ensemble of atoms* may excite and deexcite them in many ways *simultaneously*. Thus contributions of many frequencies are always present [see Fig. 1(a)]. One has a unique source of ω light but several detectors for beams of different frequencies: 2ω, 3ω, etc., resulting from sum frequency generation (in particular SHG); linearly propagating ω light; and a dc current resulting from difference frequency generation. This is due to the expansion of the source term (polarization $\mathbb{P}$) in terms of the electric field:

$$\mathbb{P} = \mathbf{P_1} + \mathbf{P_2} + \cdots = \chi^{(1)}(\omega)\mathbf{E}^{(\omega)} + \chi^{(2)}(\omega) : \mathbf{E}^{(\omega)}\mathbf{E}^{(\omega)} + \ldots . \tag{6}$$

Imposing time reversal, the detectors become sources and vice versa. Thus, in the time reversed process, one ends up with a single detector, the one which receives the light of frequency ω [Fig. 1(b)]. In order to obtain this single frequency one has to redirect all these (previously generated) beams back to the sample, conserving their phases. The source term now becomes

$$\mathbb{P} = \chi^{(1)}(\omega)\mathbf{E}^{(\omega)} + \chi^{(1)}(2\omega)\mathbf{E}^{(2\omega)} + \cdots + + \chi^{(2)}(\omega) : \mathbf{E}^{(\omega)}\mathbf{E}^{(\omega)} + \chi^{(2)}(\mathbf{2\omega}) : \mathbf{E}^{(2\omega)}\mathbf{E}^{(2\omega)} + \ldots . \tag{7}$$

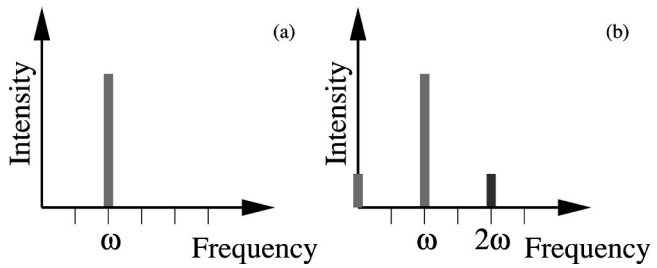

FIG. 2. Light intensity distribution on the input (a) and on the output (b) of the SHG.

Since the phases of the now incident electric fields are the same as for the previously outgoing electric fields, all the terms but those with $\chi^{(1)}$ cancel (which means that in the outgoing light one now has only the contribution at the frequency ω) and the original situation at the input of the process is restored. This description, though mathematically correct, is physically invalid, since there is no practical way to detect an infinite array of frequencies along with the phases and to revert it with arbitrary accuracy [Fig. 1(c)]. Tracing out the ''bath'' degrees of freedom (frequencies other than ω and 2ω) causes a transition from a pure to a mixed state of the system, which means that some memory is lost. This happens because the traced subsystem and the bath are not statistically independent.[23] Thus, in any practical situation, there is no possibility to generate only the frequency ω out of a whole array of frequencies. The process of SHG looks different in $(-t)$ than in (t). Such a process is called *dynamical*.

As stated before, there is no dissipation in the process of SHG in the usual meaning, i.e., the amount of energy in the radiative form is constant. However, there is a transfer of energy between the frequencies, in particular energy flows from the frequency ω to other frequencies (see Fig. 2). We call this *dissipation in frequency space*, in contrast to the more usual *dissipation in real time*. Dissipation in frequency space can mix real and imaginary parts of the nonlinear susceptibility tensor. The distinction between these two types of dissipation is often encountered in the literature. We consider them here on an equal footing stating that the presence of any of them (in our case it is the dissipation in frequency space) causes the system to have dynamical and thus irreversible properties. In this case, time reversal does not apply to the symmetry analysis.[13,14,24]

So far we have reasoned that the time-reversal operation has to be excluded from the symmetry analysis of SHG. However, *magnetism* may bring an additional complication, since the magnetic spin structure is an additional aspect the symmetry analysis must account for, and it is the time reversal which is conveniently applied to flip the local magnetic moments. This is, however, not correct: it is the classical covering symmetry[28] of the magnetic crystal which should be addressed in a symmetry analysis rather than the quantum-mechanical symmetry of the wave functions.[29] This means that the operation applied to reverse the localized magnetic moments should be performed in real space rather than Hilbert spin space. Consequently, time reversal cannot be used for the symmetry classification of magnetic moments.

Taking into account that time reversal is not suitable for the description of dynamical phenomena, one needs an op-

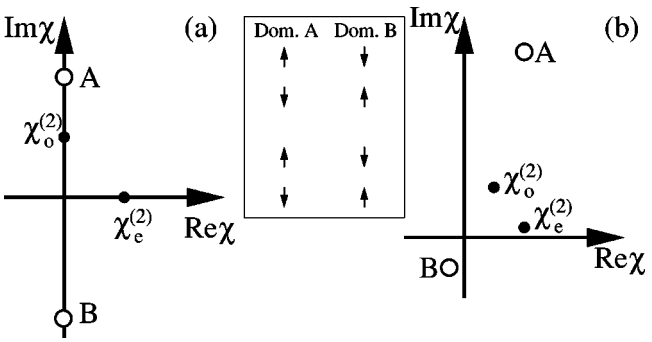

FIG. 3. Nonlinear susceptibility tensor elements and resulting SHG intensity using time reversal [panel (a)] and spin reversal [panel (b)]. Position of the points ''A'' and ''B'' is given by $(\chi_e^{(2)})^2+(\chi_o^{(2)})^2\pm 2\chi_e^{(2)}\cdot\chi_o^{(2)}$, and the distance of the points ''A'' and ''B'' from the origin of the complex plane corresponds to the intensity of SHG from the domains A and B, respectively (see inset for an example of domains in Cr_2O_3). For simplicity, the moduli of the tensor elements have been taken as equal to 1, but the argumentation also holds in the general case.

eration which merely flips the localized magnetic moments without inverting the time flow. This can be accomplished by purely spatial point-group operations. In many *antiferromagnetic* crystals a simple translation by a lattice vector reverses the magnetic moments. In many ferromagnetic and antiferromagnetic systems this may be accomplished by a mirror operation. The spatial operation, which reverses the localized magnetic moments, is called by us ''moment reversal.'' This operation is obviously unitary, in contrast to the time-reversal operation. Consequently, one does not need to invoke the time-reversal operation to describe the full symmetry of magnetic crystals.

Next, we support our reasoning by an example where the application of time reversal and ''moment-reversal'' in the symmetry analysis yields different results (see Fig. 3). Let us assume a spin structure with two domains, A and B, related to each other by spin reversal.[26] A symmetry analysis, similar to the one in Ref. 27, provides us with the set of nonvanishing elements of the nonlinear susceptibility tensor (i.e., $\chi^{(2)}$ tensor) along with the parities of these elements. Let us assume that for a certain experimental geometry only two tensor elements, called $\chi_o^{(2)}$ and $\chi_e^{(2)}$, contribute to the resulting SHG light, and that $\chi_o^{(2)}$ is odd while $\chi_e^{(2)}$ is even in the domain operation. The intensity of SHG light at a fixed polarization is given by

$$I_p\sim|(\chi_e^{(2)})^2+(\chi_o^{(2)})^2\pm 2\chi_e^{(2)}\cdot\chi_o^{(2)}| \tag{8}$$

where ''+'' stands for domain A, ''−'' for domain B. In the conventional approach, where *time reversal* is the operation mapping domains into each other, $\chi_o^{(2)}$ must be purely imaginary and $\chi_e^{(2)}$ purely real [Fig. 3(a)], since the operation of time reversal is antiunitary.[25] In this traditional approach, the first two components of the sum in Eq. (8) are real, while the last one is imaginary. Because it is the modulus of the whole sum that determines the output intensity, the domain contrast is lost since

$$|a+ib|=|a-ib|. \tag{9}$$

This is not the case if one uses the spatial operation of ''moment reversal'' for the symmetry classification, since then both tensor elements $\chi_o^{(2)}$ and $\chi_e^{(2)}$ are just complex numbers without any constraints on their relative phase, see Fig. 3(b), and domain imaging is possible, as described in Ref. 27. Consequently, the symmetry analysis yields very different predictions if one uses time or spin reversal. In the limit far from resonances, however, the phase difference between $\chi_o^{(2)}$ and $\chi_e^{(2)}$ approaches 90°, and the domain contrast is lost also in the ''moment-reversal'' description (in agreement with experiment[12]).

Finally we would like to remark on the validity of previous work on the group-theoretical classification of (magneto-)optical tensors. According to Pan *et al.*,[10] the time-reversal operation, because of its antiunitarity, forces the tensor elements to decouple into mutually exclusive sets of purely real and imaginary ones (if all kinds of dissipation are neglected). In addition, the crystal symmetry forces the tensor elements to decouple into mutually exclusive sets of elements odd and even in *magnetization* reversal, these two divisions are equivalent in the absence of conventional dissipation, i.e., real (imaginary) elements are even (odd) in the magnetization. These are the results of a purely quantum-mechanical approach, where the Hamiltonian is Hermitian (nondissipative). However, the nonlinear susceptibility tensor describes the observed process of SHG, and thus one should not apply uniquely microscopic conclusions to the analysis of these tensor elements. Consequently, taking into account the dissipation in frequency space (i.e., redistribution of the response frequencies), will prevent the classification of tensor elements as purely real or imaginary ones, although for systems with higher symmetry the classification of tensor elements as odd and even ones in the magnetization (or in the antiferromagnetic order parameter **L**) can still apply.[30]

In summary, we have shown that the time-reversal operation, often used for the symmetry classification of magneto-optical phenomena, in general cannot be applied to nonlinear optics. It should rather be replaced by spatial operations, resulting then in a proper description of the phenomena.

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[22] Both ω and 2ω beams can be attenuated during their propagation, but this is merely dissipation in the linear propagation of the wave through a medium. In our analysis, we neglect this kind of dissipation. Under this condition, linear optics is reversible. This can be seen for example in the Faraday effect, which (in the absence of dissipation) consists only of the rotation of the polarization plane (no induced ellipticity). After applying the time-reversal operation, the polarization of the light at the output (of the reversed process) is the same as the polarization at the input of the original process, thus time-reversal symmetry is preserved. This is true if one follows our convention and applies the time reversal *both* to the sample and to the measurement process.
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[29] According to Ref. 28, both the σ_x and σ_y operations cause reversal of the spin part of the quantum-mechanical fermionic wave function. Of them, σ_y is conveniently used to describe time reversal, since it is an antiunitary operation.
[30] The nonlinear susceptibility tensor $\chi^{(2\omega)}$ was usually approximated to be real far from resonances. This approximation is not valid in the systems described by us: metals and transition-metal oxides, where at any frequency one is close enough to one of the resonances (at least outside the gap of the latter). The crystals previously mostly used for SHG, and even more extensively as textbook examples, were usually wide-band-gap insulators and one is frequently far from any resonance.