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Inverse magnetochiral birefringence

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When a coherent beam of light of arbitrary polarization travels in a medium composed of randomly oriented chiral (parity-broken) particles, it is predicted to induce a constant magnetization parallel or antiparallel to the direction of propagation. Under normal laboratory conditions the induced magnetization should be very weak, yet detectable by modern means of measurement. This nonlinear-optical effect, which we name "inverse magnetochiral birefringence," has the opposite sign for enantiomers. It is a difference-frequency effect related to optical rectification or to the inverse Faraday effect.

I. INTRODUCTION

The description of the nonlinear-optical properties of matter is usually based on time-dependent perturbation theory.[1–3] The frequency-dependent moments induced by the radiation field may then be expressed in terms of multiple sums over all eigenstates of the unperturbed system. The individual terms in these sums contain in the numerators products of matrix elements of the system-field interactions. In the expressions for the denominators there appear the transition energies of the system, the frequencies of the radiation field, and appropriate damping factors. If one is primarily interested in symmetry properties and polarization effects, it is then sufficient to merely consider the numerators. In the following we assume that our system is composed of randomly oriented chiral particles, i.e., of a gas or fluid of particles in which parity is broken. We disregard effects due to resonances.

For the induced polarization due to the nonlinear optical phenomena of sum- or difference-frequency generation, $\mathbf{P}^{(2)}(\omega_1 \pm \omega_2; -\omega_1, \mp\omega_2)$, the numerators have, omitting constant factors, the general form

$$\boldsymbol{\mu}(\boldsymbol{\mu}'\cdot{}^1\mathbf{E}_-)(\boldsymbol{\mu}''\cdot{}^2\mathbf{E}_\mp)\ , \tag{1}$$

where $\boldsymbol{\mu}$, $\boldsymbol{\mu}'$, and $\boldsymbol{\mu}''$ designate matrix elements of the electric dipole operator and are, without loss of generality, assumed to be real. ${}^1\mathbf{E}_\mp, {}^2\mathbf{E}_\mp$ denote (complex) electric field vectors of the radiation of frequencies ω_1 and ω_2, respectively, taken at the origin of the multipole expansion of the particle-field interaction.[4] Upon isotropic averaging[5], expression (1) splits up into a factor pertaining to the particle susceptibility times a field factor, and is then proportional to

$$(\boldsymbol{\mu}\cdot\boldsymbol{\mu}'\times\boldsymbol{\mu}'')({}^1\mathbf{E}_-\times{}^2\mathbf{E}_\mp)\ . \tag{2}$$

We notice that the susceptibility is odd with respect to parity and only fails to vanish in optically active (parity-broken) media. If $\omega_1=\omega_2$ and ${}^1\mathbf{E}_\mp={}^2\mathbf{E}_\mp$, then the field factor for second-harmonic generation, $\mathbf{E}_-\times\mathbf{E}_-$ or $\mathbf{E}_+\times\mathbf{E}_+$, vanishes.[2] For optical rectification, the product $\mathbf{E}_-\times\mathbf{E}_+$ only fails to vanish if the electric vector is complex, i.e., the radiation is circularly polarized [Fig. 1(a)]. However, the cross product of the vector $\mathbf{E}_-$ with its complex conjugate $\mathbf{E}_+$ is then imaginary. If the susceptibility is real, which we may assume, then the induced polarization $\mathbf{P}_2(0;-\omega,+\omega)$ is imaginary.

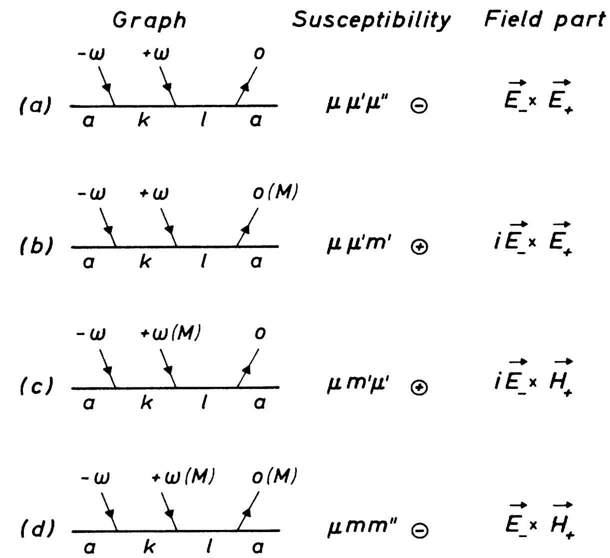

FIG. 1. Generalized graphs and expressions for the induced polarization. The susceptibility, as represented, may in all cases be considered as a real quantity. Its transformation properties under the parity operator depend on the number of electric $\boldsymbol{\mu}$ (odd) and magnetic $\mathbf{m}=i\mathbf{m}'$ (even) dipole matrix elements entering a given expression. The field part, as indicated, after isotropic averaging, determines if the resulting induced polarization is real; see also Ref. 5. (a) Optical rectification. The susceptibility is odd with respect to parity. The field part is zero or imaginary. (b) Inverse Faraday effect. The susceptibility is even with respect to parity. The field part is real. The effect is circular differential. (c) This hypothetical effect consists of an electric polarization being induced by the combination of an electric dipole and a magnetic dipole interaction with the radiation field. The field part turns out to be imaginary. (d) Inverse magnetochiral birefringence. The susceptibility is odd with respect to parity. The field part is real, making the effect as a whole real. The effect is not circular differential, but polarization independent.

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On the other hand, the corresponding magnetic effect [Fig. 1(b)] may lead to a real observable. The induced magnetization $\mathbf{M}^{(2)}(0;-\omega,+\omega)$ depends on quantities of the form

$$\mathbf{m}(\boldsymbol{\mu}\cdot\mathbf{E}_-)(\boldsymbol{\mu}'\cdot\mathbf{E}_+) \ . \tag{3}$$

The vector $\mathbf{m}$ represents a matrix element of the magnetic dipole operator. We assume, without loss of generality, that it is imaginary and may be written as $\mathbf{m}=i\mathbf{m}'$, where $\mathbf{m}'$ is real. Upon isotropic averaging we are led to the expression

$$(\mathbf{m}'\cdot\boldsymbol{\mu}\times\boldsymbol{\mu}')(i\mathbf{E}_-\times\mathbf{E}_+) \ . \tag{4}$$

Both the susceptibility and, assuming circularly polarized light, the field factor are real quantities. We notice that the susceptibility is even with respect to parity. Setting[5]

$$\mathbf{E}_{\mp}=\frac{\epsilon}{2}(\mathbf{i}\pm i\mathbf{j}) \ , \tag{5}$$

which corresponds to a left circularly polarized beam propagating in the $\mathbf{k}$ direction, we find

$$i\mathbf{E}_-\times\mathbf{E}_+=\frac{\epsilon^2}{2}\mathbf{k} \ . \tag{6}$$

To second order in the interaction with the system, the circularly polarized radiation induces a static magnetic moment parallel to the direction of propagation. For a right circularly polarized beam, the sign of the induced magnetic moment is reversed. This phenomenon, known as the "inverse Faraday effect,"[6-9] has been indeed observed.[7,8] The inverse Faraday effect is related to the "ordinary" Faraday effect in a similar manner as optical rectification is related to the linear electro-optic effect. But because of the fundamental difference between polar electric vectors and axial magnetic vectors, the magnetic effects considered here and their purely electric counterparts are observed under very different conditions.

II. INVERSE MAGNETOCHIRAL BIREFRINGENCE

The aim of the present investigation is to consider nonlinear, second-order optical effects which are similar to the ones mentioned in Sec. I, but in which a magnetic dipole (or electric quadrupole) interaction of the system with the radiation field occurs. The situation represented by Fig 1(c) corresponds to an induced electric polarization $\mathbf{P}^{(2)}(0,-\omega,+\omega(M))$ arising from terms of the form

$$\boldsymbol{\mu}(\boldsymbol{\mu}'\cdot\mathbf{E}_-)(\mathbf{m}\cdot\mathbf{H}_+) \ . \tag{7}$$

This leads, upon isotropic averaging, to the product of a real susceptibility factor times a field factor

$$(\boldsymbol{\mu}\cdot\boldsymbol{\mu}'\times\mathbf{m}')(i\mathbf{E}_-\times\mathbf{H}_+) \ , \tag{8}$$

where, as before, we have set $\mathbf{m}=i\mathbf{m}'$. We examine the field part, considering, as in expression (5), a left-circularly-polarized beam. The corresponding magnetic vector is written

$$\mathbf{H}_{\mp}=\frac{\epsilon}{2}(\mp i\mathbf{i}+\mathbf{j}) \ . \tag{9}$$

It is then immediately seen that $\mathbf{P}^{(2)}(0,-\omega,+\omega(M))$ becomes imaginary and that it therefore cannot be observed under the specified conditions.

Figure 1(d) represents an induced magnetic polarization $\mathbf{M}^{(2)}(0,-\omega,+\omega(M))$ arising from terms of the form

$$\mathbf{m}(\boldsymbol{\mu}\cdot\mathbf{E}_-)(\mathbf{m}''\cdot\mathbf{H}_+) \ , \tag{10}$$

leading, upon isotropic averaging, to

$$(\mathbf{m}\cdot\boldsymbol{\mu}\times\mathbf{m}'')(\mathbf{E}_-\times\mathbf{H}_+) \ . \tag{11}$$

$\mathbf{m}$ and $\mathbf{m}''$ are imaginary matrix elements of the magnetic dipole operator. The susceptibility is therefore real; so also is the field part. Consequently, $\mathbf{M}^{(2)}(0,-\omega,+\omega(M))$ is a real observable. The effect requires an optically active (chiral, or parity-broken) medium to occur. As may be easily verified, it has the *same* sign for a left as for a right-circularly-polarized beam. For its occurrence, it therefore does not depend on the polarization of the incident radiation. However, it has the opposite sign for optical enantiomers. This effect is related to magnetochiral birefringence[10-12] in the same way as the inverse Faraday effect is related to magnetic circular birefringence. We therefore propose the name "inverse magnetochiral birefringence."

III. DIAMAGNETIC AND PARAMAGNETIC CONTRIBUTIONS

We now compare the quantum-mechanical expressions for the diamagnetic and paramagnetic contributions to the inverse magnetochiral birefringence, $\mathbf{M}^{(2)}(0;-\omega,+\omega(M))$, with those for the inverse Faraday effect,[6-9] $\mathbf{M}^{(2)}(0,-\omega,+\omega)$.

The dominant diamagnetic terms may be obtained from the sum-over-states expressions for optical rectification,[2] by selective substitution of some of the electric dipole matrix elements by corresponding magnetic dipole elements. After isotropic averaging and some rearrangements one then gets

$$\mathbf{M}^{(2)}(0;-\omega,+\omega(M))=\frac{N\omega}{3\hbar^2}\sum_k\sum_l\left[(\boldsymbol{\mu}_{ka}\cdot\mathbf{m}_{al}\times\mathbf{m}_{lk})\frac{\omega(\omega_{la}+\omega_{ka})}{\omega_{la}(\omega_{la}^2-\omega^2)(\omega_{ka}^2-\omega^2)}-(\boldsymbol{\mu}_{lk}\cdot\mathbf{m}_{ka}\times\mathbf{m}_{al})\frac{(\omega_{la}+\omega_{ka})}{2\omega_{la}\omega_{ka}(\omega_{la}-\omega)(\omega_{ka}+\omega)}\right](\mathbf{E}_-\times\mathbf{H}_+) \ . \tag{12}$$

As already mentioned, we assume in the diamagnetic case the wave functions of all states, a,k,l of the system (molecule) to be real. Products of the type $\mathbf{m}_{al}\times\mathbf{m}_{lk'}$ etc., are therefore real quantities.

The corresponding expression for the diamagnetic contribution to the inverse Faraday effect is found to be

$$\mathbf{M}^{(2)}(0;-\omega,+\omega)=-i\frac{N\omega}{3\hbar^2}\sum_k\sum_l\left[\mathrm{Im}(\boldsymbol{\mu}_{ka}\cdot\mathbf{m}_{al}\times\boldsymbol{\mu}_{lk})\frac{2}{\omega_{la}(\omega_{ka}^2-\omega^2)}-\mathrm{Im}(\mathbf{m}_{lk}\cdot\boldsymbol{\mu}_{ka}\times\boldsymbol{\mu}_{al})\frac{(\omega_{la}+\omega_{ka})}{(\omega_{la}^2-\omega^2)(\omega_{ka}^2-\omega^2)}\right](\mathbf{E}_-\times\mathbf{E}_+)\ . \quad (13)$$

Notice the factor i which makes the whole expression real for a circularly polarized light beam.

To obtain the paramagnetic contributions, we consider a system with a degenerate ground state, expressed by the wave functions $a_+=\Psi_+(t=0)$ and $a_-=\Psi_-(t=0)$. $a_+=(a_-)^*$. In the presence of the radiation field the degeneracy gets lifted in second order. The states are then written as $\Psi_+(t)$ and $\Psi_-(t)$. The quantity of interest is the ground-state magnetization, which, in the absence of other influences, is due to the lifting of the degeneracy by the interaction with the radiation

$$N_+\langle\Psi_+|\mathbf{m}|\Psi_+\rangle+N_-\langle\Psi_-|\mathbf{m}|\Psi_-\rangle\ . \quad (14)$$

Depending on the polarization this magnetization contains a contribution due to the inverse Faraday effect $\mathbf{M}^{(2)}(0;-\omega,+\omega)$, as well as a contribution due to the inverse magnetochiral birefringence $\mathbf{M}^{(2)}(0;-\omega,+\omega(M))$. N_+ and N_- represent the respective populations of the two states. $N_++N_-=N$. In a steady-state situation, the molecular system is supposed to be in thermal equilibrium with its surroundings:

$$N_+/N_-=\exp(-\Delta E/kT)\ ,$$
$$\Delta E=\langle\Psi_+|\mathcal{H}|\Psi_+\rangle-\langle\Psi_-|\mathcal{H}|\Psi_-\rangle\ . \quad (15)$$

$\mathcal{H}$ denotes the (semiclassical) Hamiltonian for the system in the radiation field. To a first and satisfactory approximation, (14) may be set equal to

$$(N_+-N_-)\langle a_+|\mathbf{m}|a_+\rangle\ . \quad (16)$$

The quantity of interest is then ΔE, which, like the diamagnetic effects considered previously, is calculated by elementary time-dependent perturbation theory using a steady-state ansatz. Neglecting higher-order terms one obtains for the paramagnetic contribution to the inverse magnetochiral birefringence,

$$\mathbf{M}^{(2)}(0;-\omega,+\omega(M))=\frac{2N}{3kT\hbar}\sum_k{}'\left[\mathbf{m}_{aa}\cdot\mathrm{Re}(\boldsymbol{\mu}_{ak}\times\mathbf{m}_{ka})\frac{\omega_{ka}}{(\omega_{ka}^2-\omega^2)}\right]\times(\mathbf{E}_-\times\mathbf{H}_+)\ . \quad (17)$$

In this expression a stands either for a_+ or a_- and denotes a complex wave function. The analogous expression for the paramagnetic contribution to the inverse Faraday effect is found to be

$$\mathbf{M}^{(2)}(0;-\omega,+\omega)=-i\frac{2N}{3kT\hbar}\sum_k{}'\left[\mathbf{m}_{aa}\cdot\mathrm{Im}(\boldsymbol{\mu}_{ak}\times\boldsymbol{\mu}_{ka})\frac{\omega}{(\omega_{ka}^2-\omega^2)}\right]\times(\mathbf{E}_-\times\mathbf{E}_+)\ . \quad (18)$$

Notice the T^{-1} dependence of the paramagnetic terms (17) and (18). Expressions for the inverse Faraday effect equivalent to (13) and (18) have been derived by Atkins and Miller.[9]

IV. DISCUSSION

One may estimate the magnetization induced by the inverse Faraday effect with a radiation field intensity of 10^8 W cm^{-2}, such as is easily attainable with a pulsed laser, to be of the order of 10^{-6} G. Induced magnetizations of 10^{-5} G have indeed been measured.[7] The magnetization due to the inverse magnetochiral birefringence in a molecular system should be smaller by the order of $(e\hbar/2mc)/ea_0$ in cgs units. This corresponds to a magnetization of 10^{-9}–10^{-8} G, a magnetic induction of 10^{-8}–10^{-7} G, or 10^{-12}–10^{-11} T. Superconducting-quantum-flux sensors offer nowadays the possibility of measuring magnetic fields of the order of 10^{-10} G, i.e., inductions of 10^{-14} T.[13] In biomagnetism, magnetic inductions as small as 10^{-15} T have proven to be detectable.[14] This suggests that the magneto-optic effect discussed here should also be accessible to measurements.

The inverse magnetochiral birefringence should not only arise through the combination of electric dipole and magnetic dipole interactions with the radiation field, as described in Secs. II and III, but also via electric-dipole–electric-quadrupole contributions.[11,12,15] The expressions corresponding to (12) and (17) are obtained by appropriately replacing in every term of the summations one of the magnetic dipole matrix elements by a similar electric quadrupole element.

Magnetochiral birefringence and dichroism are effects which reflect fundamental symmetry properties of the interaction of matter with radiation when parity-breaking influences occur.[11,16–19] Similar basic symmetry considerations should apply equally to the inverse phenomenon discussed here: The chiral fluid sample and the propagation vector of light considered relative to each other transform under space inversion and time reversal as a time-odd axial vector, i.e., as a magnetic field.

It should furthermore be pointed out that the effect is not tied to a single order in the multipole expansion of the molecule-field interaction. Higher-order interactions may be identified, such as magnetic-dipole–magnetic-quadrupole, which should also contribute. Whenever the long-wavelength approximation is fulfilled, these higher-order terms play a diminishing role. Neither does the effect under consideration only occur to second order in the optical nonlinearity. One finds progressively smaller contributions to fourth and higher (even) order, such as $\mathbf{M}^{(4)}(0;-\omega,+\omega,-\omega,+\omega(M))$, etc.

V. CONCLUSIONS

It is concluded that a beam of light of arbitrary polarization traveling in a medium of randomly oriented chiral (parity-broken) particles (molecules) should, to second (and possibly higher) order(s) in the interaction between radiation and matter, induce a constant magnetization parallel or antiparallel to the direction of propagation. In a molecular system under laboratory conditions the effect should be very weak, yet detectable. It should reverse its sign for optical enantiomers.

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