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Chapter 13

MAGNETOELECTRO-OPTICS

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I. INTRODUCTION

Michael Faraday, in 1846 [1], discovered to the surprise of his contemporaries that a dc magnetic field affects directly the optical properties of matter. He showed that, when polarized light traverses matter in a direction parallel to that of an externally applied magnetic field, the polarization plane of the light wave is rotated by an angle θ proportional to the path l traversed in the layer of the substance and to the magnetic field strength H:

$$\theta = V(\lambda) l H \tag{1}$$

$V(\lambda)$ denoting the magneto-optical rotation constant or Verdet constant [2], dependent on the nature of the medium, the temperature, and wavelength λ of the incident light.

By Fresnel's theory [3], plane-polarized (linearly polarized) light has to be regarded as a superposition of two circularly polarized waves of the same wavelength and amplitude. The rotation of the plane of polarization is then due to a difference between the refractive indexes n_+ and n_- of the optically activated medium for right and left circularly polarized waves, at the circular frequency $\omega = 2\pi c/\lambda$. In Faraday's effect the optically inactive medium becomes active under the influence of the dc magnetic field, and we can write the following relation for the amount of magneto-optical rotation:

$$n_+ - n_- = \frac{2c}{\omega} V(\lambda) H = \frac{\lambda}{\pi} V(\lambda) H \tag{2}$$

Optical activity, induced in matter by an externally applied magnetic field, is to be distinguished from natural optical activity. The latter is an intrinsic property of media as a result of molecular, or crystalline, optical asymmetry.

If the light propagates at right angles to the magnetic field (Voigt configuration [4]), the naturally isotropic medium -- as was first shown by Majorana [5] in colloidal solutions and subsequently by Cotton and Mouton [6] in liquids -- becomes optically birefringent with optical axis parallel to the direction of the magnetic field. Similarly, to Kerr's effect, the amount of this magnetically induced birefringence is given by the difference between the refractive indexes for component light vibrations parallel and perpendicular to the direction of the applied field H:

$$n_{\parallel} - n_{\perp} = \lambda C(\lambda) H^2 \tag{3}$$

where $C(\lambda)$ is the Cotton-Mouton constant specific to the medium, its thermodynamical state, and the light wavelength.

One of the earliest theoretical explanations of magneto-optical phenomena was proposed by Voigt [4] on the basis of Lorentz's [7] electron theory of matter. Voigt interpreted magnetically induced birefringence as due to the direct action of the magnetic field on the electrons of atoms and molecules, which undergo an anisotropic distortion proportional to the square of the field strength H in accordance with the law (3). By Voigt's theory, the absolute retardation ratio should be:

$$\frac{n_{\parallel} - n}{n_{\perp} - n} = +3 \tag{3a}$$

whereas the majority of experiments led to Havelock's relation [8]:

$$\frac{n_{\parallel} - n}{n_{\perp} - n} = -2 \tag{3b}$$

which results from Langevin's theory [9] of statistical molecular orientation.

Magneto-optical phenomena are unremittingly under study and have by now become the subject matter of monographs [10-17] and numerous review articles [18-23]. Work on the Faraday effect provides data on the influence of a linear (first power in H) magnetic field on atoms and molecules [24,25], macromolecules [26] and biomacromolecules [27]. Magnetic anisotropies of molecules and macromolecules, as well as their nonlinear magneto-optical properties, can be determined from Cotton-Mouton studies in rarefied gases [28], real gases and liquids [29], liquid molecular solutions [30], polymer and biopolymer solutions [31], and colloids [32].

Rapid progress in laboratory techniques has recently provided us with new sources of light in the form of gas and crystal lasers [33] and, concomitantly, with new methods of producing intense pulsed magnetic fields [34]. Thus, conditions now favor the search for new magneto-optical effects, arising under the simultaneous action of strong electric and magnetic fields, both static and rapidly alternating. Such nonlinear magneto-electro-optical effects, making apparent the direct and simultaneous action of strong magnetic and electric fields on matter, can be observed in molecular, macromolecular, and biological substances [35], and in particular in semiconducting, magnetic, and metamagnetic materials [36], crystalline bodies [14,37], and liquid crystals [38]. Among the new nonlinear effects, we shall choose for discussion here the inverse Faraday effect [39], the dc electric field effect on laser beam induced changes in magneto-optical birefringence and rotation [40], generation of laser light harmonics by magnetized bodies [41,42] as well as generation processes and frequency mixing processes in crossed electric and magnetic fields.

Strictly, the theory of magneto-optical phenomena would require a quantum-mechanical approach. However, since this article is aimed essentially at a concise presentation, or enumeration, of new magneto-electro-optical effects (besides the already known ones) and at pointing out the experimental conditions and materials in which they can be detected, we shall be resorting to a simpler, phenomenological treatment. It will moreover be our aim to draw the reader's attention to the information to be gleaned from these new effects with regard to the electro-magnetic properties of molecules, macromolecules, and colloidal particles.

II. LINEAR MAGNETOELECTRIC PROCESSES

The light refractive index n of an isotropic medium is related to the latter's electric permittivity $\varepsilon(\omega)$ and magnetic permittivity $\mu(\omega)$ at a given circular frequency ω by the well-known Maxwell relation:

$$n^2 = \varepsilon(\omega)\mu(\omega) \tag{4}$$

In naturally anisotropic bodies, the electric and magnetic properties are described by the second-rank tensors ε_{ij} and μ_{ij}, defined by the equations:

$$(\varepsilon^{\omega}_{ij} - \delta_{ij})E_j(\underline{r},t) = 4\pi P^e_i(\underline{r},t)$$

$$(\mu^{\omega}_{ij} - \delta_{ij})H_j(\underline{r},t) = 4\pi P^m_i(\underline{r},t) \tag{5}$$

where we have applied the summation convention over the recurring index j (running through the values x,y,z of axes of the laboratory Cartesian reference system). δ_{ij} is Kronecker's symmetric unit tensor.

The vectors of electric polarization $\underline{P}^e(\underline{r},t)$ and magnetic polarization $\underline{P}^m(\underline{r},t)$ are in general functions of the electric vector $\underline{E}(\underline{r},t)$ and magnetic vector $\underline{H}(\underline{r},t)$ of the electromagnetic field of the light wave existing at the moment of time t and space point $\underline{r}$. In a first approximation, the relations between these vectors are linear ones, and in a phenomenological treatment we can write:

$$P^e_i(\underline{r},t) = \chi^{ee}_{ij}E_j(\underline{r},t) + \chi^{em}_{ij}H_j(\underline{r},t) \tag{6}$$

$$P^m_i(\underline{r},t) = \chi^{mm}_{ij}H_j(\underline{r},t) + \chi^{me}_{ij}E_j(\underline{r},t) \tag{7}$$

where χ^{ee}_{ij} is the tensor of electric susceptibility and χ^{mm}_{ij} that of magnetic susceptibility of the medium. These tensors describe linear processes of light refraction and propagation in optically transparent media and media exhibiting frequency dispersion and spatial dispersion [37].

The axial tensor of cross susceptibility χ_{ij}^{em} describes the electric polarization (a polar vector) induced in the medium by a magnetic field (an axial vector). This linear magneto-electric effect has, as yet, not been observed successfully in molecular substances [10,43] but has been studied in piezoelectric paramagnetic crystals [44] and, more recently, in metamagnetic ones [45]. The inverse effect, consisting in the induction of magnetic polarization by an electric field, is described by the axial tensor χ_{ij}^{me} of cross susceptibility (in particular, $\chi_{ij}^{em} = \chi_{ji}^{me}$).

The fundamental equations (5) are also applicable to isotropic bodies, in which the respective anisotropies to be discussed in subsequent subsections are induced by an external electric, magnetic, or electromagnetic field.

III. QUADRATIC CROSS PROCESSES

In addition to the linear magneto-electric processes occurring in electric magnetic fields of low intensity, we have to consider nonlinear cross (or mixing) processes, caused by intense fields. In particular, in a second approximation, we have to deal with the electric polarization:

$$P_i^e(\underline{r},t) = \chi_{ijk}^{eem} E_j(\underline{r},t) H_k(\underline{r},t) \tag{8}$$

where χ_{ijk}^{eem} is a third-rank axial tensor describing nonlinear magneto-electric susceptibility of the second order. This tensor is of interest in that it possesses nonzero tensor elements in all media, including the isotropic medium (see Table 1).

TABLE 1

The Number of Nonzero (N) and Independent (I) Elements of Nonlinear Susceptibility Axial Tensors χ_{ijk}, χ_{ijkl}, and χ_{ijklm} for Crystallographical Classes

	$\chi^{eem}_{(ij)k}$		$\chi^{eem}_{[ij]k}$		$\chi^{eeem}_{(ij)k,l}$		$\chi^{eeem}_{[ij]k,l}$		$\chi^{eeeem}_{(ij)k,l,m}$		$\chi^{eeeem}_{[ij]k,l,n}$	
Class	N	I	N	I	N	I	N	I	N	I	N	I
1 (C_1)	27	18	18	9	81	54	54	27	243	162	162	81
$\bar{1}$ (C_i)	27	18	18	9	0	0	0	0	243	162	162	81
m (C_s)	13	8	10	5	40	26	28	14	121	80	82	41
2 (C_2)	13	8	10	5	41	28	26	13	121	80	82	41
2/m (C_{2h})	13	8	10	5	0	0	0	0	121	80	82	41
222 (D_2)	6	3	6	3	21	15	12	6	60	39	42	21
mm2 (C_{2v})	6	3	6	3	20	13	14	7	60	39	42	21
mmm (D_{2h})	6	3	6	3	0	0	0	0	60	39	42	21
4 (C_4)	11	4	10	3	39	14	26	7	119	40	82	21
$\bar{4}$ (S_4)	11	4	10	3	40	14	24	6	119	40	82	21
4/m (C_{4h})	11	4	10	3	0	0	0	0	119	40	82	21
422 (D_4)	4	1	6	2	21	8	12	3	58	19	42	11
4mm (C_{4v})	4	1	6	2	18	6	14	4	58	19	42	11
$\overline{42}$m (D_{2d})	4	1	6	2	20	7	12	3	58	19	42	11
4/mmm (D_{4h})	4	1	6	2	0	0	0	0	58	19	42	11
3 (C_3)	19	6	10	3	71	18	42	9	231	54	146	27
$\bar{3}$ (S_6)	19	6	10	3	0	0	0	0	231	54	146	27
32 (D_3)	8	2	6	2	37	10	20	4	114	26	74	14
3m (C_{3v})	8	2	6	2	34	8	22	5	114	26	74	14
$\bar{3}$m (D_{3d})	8	2	6	2	0	0	0	0	114	26	74	14
6 (C_6)	11	4	10	3	39	12	26	7	119	32	82	19
$\bar{6}$ (C_{3h})	11	4	10	3	32	6	16	2	119	32	82	19
6/m (C_{6h})	11	4	10	3	0	0	0	0	119	32	82	19
622 (D_6)	4	1	6	2	21	7	12	3	58	15	42	10
6mm (C_{6v})	4	1	6	2	18	5	14	4	58	15	42	10
$\bar{6}$m2 (D_{3h})	4	1	6	2	16	3	8	1	58	15	42	10
6/mmm (D_{6h})	4	1	6	2	0	0	0	0	58	15	42	10

TABLE 1 (continued)

Class	$\chi^{eem}_{(ij)k}$ N	$\chi^{eem}_{(ij)k}$ I	$\chi^{eem}_{[ij]k}$ N	$\chi^{eem}_{[ij]k}$ I	$\chi^{eeem}_{(ij)k,l}$ N	$\chi^{eeem}_{(ij)k,l}$ I	$\chi^{eeem}_{[ij]k,l}$ N	$\chi^{eeem}_{[ij]k,l}$ I	$\chi^{eeeem}_{(ij)k,l,m}$ N	$\chi^{eeeem}_{(ij)k,l,m}$ I	$\chi^{eeeem}_{[ij]k,l,n}$ N	$\chi^{eeeem}_{[ij]k,l,n}$ I
23 (T)	6	1	6	1	21	5	12	2	60	13	42	7
m3 (T_h)	6	1	6	1	0	0	0	0	60	13	42	7
432 (O)	0	0	6	1	21	3	12	1	54	6	42	4
$\overline{43}$m (T_d)	0	0	6	1	18	2	12	1	54	6	42	4
m3m (O_h)	0	0	6	1	0	0	0	0	54	6	42	4
Y	0	0	6	1	21	2	12	1	54	3	42	3
Y_h	0	0	6	1	0	0	0	0	54	3	42	3
K	0	0	6	1	21	2	12	1	54	3	42	3
K_h	0	0	6	1	0	0	0	0	54	3	42	3

A. Magneto-Optical Effects

Assuming the magnetic field in Eq. (8) to be static, one obtains with regard to (5) and (6) the following first-order variation in electric permittivity tensor measured at the frequency ω:

$$\Delta\varepsilon^{(1)}_{ij}(\omega) = 4\pi\chi^{eem}_{ijk}(\omega)H_k(0) \tag{9}$$

If the electromagnetic wave propagates in a direction parallel to the magnetic field, assumed as acting along the z axis (Fig. 1), the nondiagonal tensor elements of (9) defining Faraday's effect yield:

$$\Delta\varepsilon_{xy}(\omega) = -\Delta\varepsilon_{yx}(\omega) = 4\pi\chi^{eem}_{xyz}(\omega)H_z(0) \tag{9a}$$

Since, for diamagnetic media, we have in approximation [10]:

$$n_+ - n_- = \frac{i\Delta\varepsilon_{xy}(\omega)}{n} \tag{10}$$

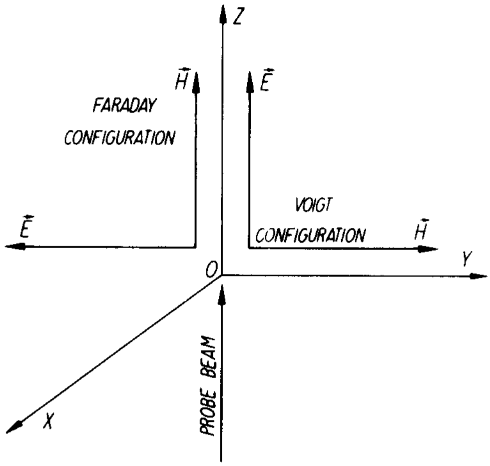

FIG. 1. Idealized experimental setup for the study of magneto-electro-optical phenomena. The probe light beam propagates along the Z axis and the molecular sample is located at the origin. The dc magnetic field H is applied either at Faraday configuration (along Z) or at Voigt configuration (along X or Y). The dc electric field E can be applied perpendicular to H (crossed fields), or parallel to H, or at any angle to H.

we find that in the case under consideration Verdet's constant given by Eq. (2):

$$V(\lambda) = \frac{4\pi^2}{n\lambda} i\chi_{xyz}^{eem}(\omega) \tag{2a}$$

is expressed by way of the magneto-electric susceptibility component $\chi_{xyz}^{eem}(\omega)$.

Recently, Ferguson and Romagnoli [46] proposed, on the basis of the magneto-electric polarization (8) and a supplementary polarization due to field gradients [47], a theory of transverse and longitudinal nonlinear Kerr magneto-optic effect in ferromagnetic metals.

B. Inverse Faraday Effect

Besides the linear magnetization by an electric field, Eq. (7), which can take place only in bodies without a center of symmetry [16], we have to deal with magnetic polarization caused by the square of an electric field [39]:

$$P_i^m(\underline{r},t) = \chi_{ijk}^{mee} E_j(\underline{r},t) E_k(\underline{r},t) \tag{11}$$

where, if the electromagnetic wave propagates in the direction of $\underline{k}$ (the wave vector), one has:

$$E(\underline{r},t) = E(\omega,\underline{k}) \exp\{i(\underline{k} \cdot \underline{r} - \omega t)\} + \text{c.c.} \tag{12}$$

We hence see that, by Eq. (11), an isotropic or indeed any other medium can undergo a magnetization not only by the square (second power) of a dc or ac electric field but, essentially, by light of intensity given by the tensor:

$$I_{jk} = \frac{E_j(\omega) E_k(-\omega)}{2} \tag{13}$$

We thus have for light beam-induced magnetization:

$$P_i^m(0) = 2\chi_{ijk}^{mee}(0) I_{jk} \tag{11a}$$

Now, considering that circularly polarized light propagating in the z direction has the amplitudes of right and left gyrating vibrations:

$$E_{\pm} = \frac{(E_x \pm iE_y)}{2} \tag{12a}$$

we obtain from Eq. (11a) the following magnetic polarization induced in a nonabsorbing material in the light propagation direction [39]:

$$P_z^m(0) = \frac{n}{2\pi^2} V(\lambda)(I_+ - I_-) \tag{14}$$

where the Verdet constant $V(\lambda)$ is defined by Eq. (2a), and I_+, I_- are intensities of right and left circularly polarized laser light. The above expression describes the inverse Faraday effect discovered by Pershan et al. [39] in diamagnetic and paramagnetic bodies illuminated with strong circularly polarized laser light.

The theory of optical magnetization of bodies was developed by Pershan et al. [39] in a phenomenological and quantum-mechanical approach, and by Kielich [48] in a molecular-statistical approach for diamagnetic and paramagnetic liquids. To Atkins and Miller [49] is due an extension of the quantum field theory of the inverse and optical Faraday effects.

C. Second Harmonic Generation

The nonlinear magneto-electric polarization (8) in conjunction with the field (12) involve, besides a constant component, a component which varies with the double frequence 2ω:

$$P_i^e(2\omega, 2\underline{k}) = \chi_{ijk}^{eem}(2\omega, 2\underline{k}) E_j(\omega, \underline{k}) H_k(\omega, \underline{k}) \tag{8a}$$

This polarization yields a magneto-electric contribution to second harmonic generation (SHG) in isotropic bodies [42], particularly metals [47], as well as to SHG at reflection from metals, semiconductors [50], and isotropic media [51].

IV. CUBIC MAGNETO-OPTICAL PROCESSES

When considering polarization processes of the third order induced by magnetic and electric fields, one comes upon a wide variety of components; for the sake of simplicity, we shall restrict ourselves here to the following one:

$$P_i^e(\underline{r},t) = \chi_{ijkl}^{eeem} E_j(\underline{r},t) E_k(\underline{r},t) H_l(\underline{r},t) \tag{15}$$

where the fourth-rank axial tensor χ_{ijkl}^{eeem} describes the nonlinear magneto-electric susceptibility of the third order. The nonzero and mutually independent elements of the tensor χ_{ijkl}^{eeem} have been calculated by Kielich and Zawodny [52] applying methods of group theory [16,53], assuming in general the presence of spatial dispersion.

A. Second-Order Magneto-Optical Birefringence and Rotation

Let us assume, in Eq. (15), one of the electric fields to be static likewise to the magnetic field. The second-order variations of the electric permittivity tensor analyzed at the frequency ω are now obtained in the form:

$$\Delta\varepsilon_{ij}^{(2)}(\omega) = 4\pi\chi_{ijkl}^{eeem}(\omega,\underline{k}) E_k(0) H_l(0) \tag{16}$$

For a further discussion of this expression, it is convenient to separate the axial tensor χ_{ijkl}^{eeem} into a symmetric part $\chi_{(ij)kl}^{eeem} = \chi_{ijkl}^{eeem} = \chi_{jikl}^{eeem}$ and a part $\chi_{[ij]kl}^{eeem} = \chi_{ijkl}^{eeem} = -\chi_{jikl}^{eeem}$ antisymmetric with respect to the indexes i and j (see Table 1). Thus, the difference between diagonal elements of the tensor (16) is:

$$\Delta\varepsilon_{xx}^{(2)}(\omega) - \Delta\varepsilon_{yy}^{(2)}(\omega) = 4\pi\{\chi_{xxkl}^{eeem}(\omega,\underline{k}) - \chi_{yykl}^{eeem}(\omega,\underline{k})\} E_k(0) H_l(0) \tag{16a}$$

whereas the difference between nondiagonal elements is:

$$\Delta\varepsilon_{xy}^{(2)}(\omega) - \Delta\varepsilon_{yx}^{(2)}(\omega) = 8\pi\chi_{xykl}^{eeem}(\omega,\underline{k}) E_k(0) H_l(0) \tag{16b}$$

Equations (16a) and (16b) describe, respectively, the optical birefringence and optical rotation induced in a medium by the simultaneous action of a dc magnetic and electric field. When proceeding to an experimental analysis of these equations, it is necessary to take into consideration the mutual configuration of the propagation direction of the analyzing light wave and the directions in which the fields $\underline{H}(0)$ and $\underline{E}(0)$ are applied in the setup chosen by the experimenter. Two limiting configurations can be distinguished, namely:

1. Faraday's configuration, in which the light wave propagates in a direction parallel to the magnetic field, and
2. Voigt's configuration, in which the light wave is directed at right angles to the magnetic field.

On taking further into consideration the various feasible spatial configurations of the dc electric field, one gets the set of experimental situations listed in Table 2 permitting the observation of new nonlinear magneto-electro-optical effects in the various crystallographical classes [54] as well as in isotropic bodies composed of molecules without a center of symmetry, and without planes of reflection symmetry [48,55]. Clearly, when planning all the details of an experiment aimed at observing this or that novel magneto-optical phenomenon, one has to calculate from Fresnel's equation the relevant refractive indexes by resorting to Eqs. (4), (5), (9), and (16).

B. Magnetic Field-Induced Second Harmonic Generation

By (12) and (15), we obtain for the polarization component induced at frequency 2ω by a dc magnetic field:

$$P_i^e(2\omega, 2\,\underline{k}) = \chi_{ijkl}^{eeem}(2\omega, 2\underline{k})E_j(\omega,\underline{k})E_k(\omega,\underline{k})H_l(0) \tag{15a}$$

Cohan and Hameka [56] proposed a quantum-mechanical theory of SHG by gases and liquids in the presence of a magnetic field. This nonlinear process is allowed in systems of randomly oriented

TABLE 2

Predicted Experimental Situations for the Observation of Second-Order Magneto-Optical Birefringence and Rotation

The analyzing light beam propagates along Z at:	Direction of dc electric field action	Magneto-Optical Birefringence [Eq. (16a)]: Relevant tensor elements $\chi^{eeem}_{(ij)kl}$	Magneto-Optical Birefringence [Eq. (16a)]: Crystallographical classes admitting of the effect	Magneto-Optical Rotation [Eq. (16b)]: Relevant tensor elements $\chi^{eeem}_{[ij]kl}$	Magneto-Optical Rotation [Eq. (16b)]: Crystallographical classes admitting of the effect
Voigt configuration (H_y)	x	xxxy - yyxy	1, 2, mm2, 4, $\bar{4}$, 4mm, 3, 3m, 6, 6mm	xyxy = -yxxy	1, 2, 222, 4, $\bar{4}$, 422, $\overline{42}$m, 3, 32, 6, 622, 23, 432, $\overline{43}$m, Y, K
	y	xxyy - yyyy	1, 2, 222, 4, $\bar{4}$, 422, $\overline{42}$m, 3, 32, 6, 622, 23, 432, $\overline{43}$m, Y, K	xyyy = -yxyy	1, 2, mm2, 4, $\bar{4}$, 4mm, 3, 3m, 6, 6mm
	z	xxzy - yyzy	1, 3, 32, $\bar{6}$, $\bar{6}$m2	xyzy = -yxzy	1, m
Faraday configuration (H_z)	x	xxxz - yyxz	1, m, 3, 3m, $\bar{6}$	xyxz = -yxxz	1, m
	y	xxyz - yyyz	1, m, 3, 32, $\bar{6}$, $\bar{6}$m2	xyyz = -yxyz	1, m
	z	xxzz - yyzz	1, 2, 222, $\bar{4}$, $\overline{42}$m, $\overline{43}$m, 23	xyzz = -yxzz	1, 2, mm2, 4, 4mm, 3, 3m, 6, 6mm

and noninteracting molecules that have neither a center of symmetry nor a plane of reflection. Kielich and Zawodny [52], on the basis of Eq. (15a), discussed SHG in all crystallographical classes and showed that a dc magnetic field induces SHG in the classes $422(D_4)$, $622(D_6)$, $432(O)$, as well as Y and K, in which SHG is forbidden at $H(0) = 0$ and fulfillment of Kleinman's symmetry conjecture [57]. Thus, experimental studies of dc magnetic field-induced SHG will surely become a powerful method of deciding the crystallographical class of bodies, as well as molecules and macromolecules, the symmetry of which cannot be determined by other methods.

Lately, Hafele et al. [58], using a high-power Q-switched CO_2 laser radiating at 10.6 μm, performed studies of the dc magnetic field dependence of SHG in InSb near the energy gap.

V. MAGNETO-OPTICAL PROCESSES OF HIGHER ORDER

Modern measuring techniques permit the investigation of higher order magneto-optical processes, such as light-intensity-dependent Faraday effect or Cotton-Mouton effect [59,60], doubling and mixing of laser light frequencies in crossed electric and magnetic fields [61], and third-harmonic generation (THG) in the presence of a dc magnetic field [62,63]. Here, we shall consider electric polarization of the fourth order, in the form:

$$P_i^e(\underline{r},t) = \chi_{ijkln}^{eeeem} E_j(\underline{r},t) E_k(\underline{r},t) E_l(\underline{r},t) H_n(r,t) \tag{17}$$

where the fifth-rank axial tensor χ_{ijkln}^{eeeem} describes nonlinear magneto-optical susceptibility of the fourth order the nonzero and independent tensor elements of which have been calculated by group theoretical methods [64]. In Table 1, we give solely the number of these elements for the partly symmetric tensor $\chi^{eeeem}_{(ij)kln}$ and the antisymmetric tensor $\chi^{eeeem}_{[ij]kln} = \chi^{eeeem}_{ijkln} - \chi^{eeeem}_{jikln}$.

A. Third-Order Magneto-Optical Birefringence and Rotation

We shall now consider the experimental situation which arises when, on a medium analyzed with light of frequency ω_A, another light beam of frequency ω_I is incident inducing optical nonlinearity. With regard to Eqs. (5) and (17), the third-order variation of the tensor of electric permittivity takes the form:

$$\Delta\varepsilon^{(3)}_{ij}(\omega_A) = 4\pi\chi^{eeeem}_{ijkln}(\omega_A,\omega_I)E_k(\omega_I)E_l(-\omega_I)H_n(0) \tag{18}$$

whence we obtain the following expressions for the light intensity-dependent magneto-optical birefringence and rotation:

$$\Delta\varepsilon^{(3)}_{xx}(\omega_A) - \Delta\varepsilon^{(3)}_{yy}(\omega_A) = 8\pi\{\chi^{eeeem}_{xxkln}(\omega_A,\omega_I) - \chi^{eeeem}_{yykln}(\omega_A,\omega_I)\}I_{kl}H_n(0) \tag{18a}$$

$$\Delta\varepsilon^{(3)}_{xy}(\omega_A) - \Delta\varepsilon^{(3)}_{yx}(\omega_A) = 16\pi\chi^{eeeem}_{xykln}(\omega_A,\omega_I)I_{kl}H_n(0) \tag{18b}$$

In Table 3 are listed the experimental setups permitting the observation of the new magneto-optical processes (18a) and (18b) at Faraday's and Voigt's configurations, for various well-defined propagation directions of the strong laser beam of intensity I.

Recently, Kubota [60] first succeeded in revealing experimentally light-intensity-dependent magneto-optical rotation in Faraday configuration in crystalline semiconductors (CdS, ZnS). In Kubota's experiment, a probe beam is obtained from a Xe flash lamp, whereas a Q-switched Nd-glass or ruby laser is used as intense light source of the frequency ω_I. Although the statistical-molecular theory of the light-intensity-dependent variations in Faraday effect in gases and liquids was proposed by Kielich

[59,65] some years ago, reports of successful experiments are still lacking.

On putting $\omega_I = 0$ in Eq. (18), one obtains an expression for the influence of the square of a dc electric field on magneto-optical effects. Obviously, when studying these effects in isotropic bodies, one has to take into account the unavoidable presence of a strong Kerr or, respectively, Cotton-Mouton effect, according to the configuration applied. In fact, we have the additional variation in permittivity tensor:

$$\Delta\varepsilon_{ij}(\omega) = 4\pi\{\chi^{eeee}_{ijkl}E_k E_l + \chi^{eemm}_{ijkl}H_k H_l + \ldots + \chi^{eeemm}_{ijklm}E_k H_l H_m + \ldots + \chi^{eeeemm}_{ijklmn}E_k E_l H_m H_n + \ldots\} \quad (19)$$

Above, the tensor of nonlinear electric susceptibility χ^{eeee}_{ijkl} defines the quadratic Kerr effect, that of magneto-electric susceptibility χ^{eemm}_{ijkl} -- a magnetically induced anisotropy [48] or the quadratic Cotton-Mouton effect, and that of magneto-electric susceptibility of order 5 χ^{eeeemm}_{ijklmn} -- the cross effect due to the direct concomitant action of electric and magnetic fields on the isotropic medium. This latter cross effect is accessible to observation in solutions of macromolecules and colloid particles, where the effects of nonlinear electron Voigt distortion are accompanied by a strong Langevin reorientation of the microsystems [40,66].

B. Doubling and Mixing in Crossed Electric and Magnetic Fields

The general formula (17) can be particularized to the form:

$$P^e_i(2\omega) = \chi^{eeeem}_{ijkln}(2\omega)E_j(\omega)E_k(\omega)E_l(0)H_n(0) \quad (17a)$$

describing SHG in the presence of dc electric and magnetic fields. The process, a general discussion of which is due to Kielich [61],

TABLE 3

Predicted Experimental Situations for the Observation of Third-Order Magneto-Optical Birefringence and Rotation

The analyzing light beam propagates along Z at:	Propagation direction of inducing laser light	Magneto-Optical Birefringence [Eq. (18a)]: Relevant tensor elements $\chi^{eeeem}_{(ij)kln}$	Magneto-Optical Birefringence [Eq. (18a)]: Classes admitting of the effect	Magneto-Optical Rotation [Eq. (18b)]: Relevant tensor elements $\chi^{eeeem}_{[ij]kln}$	Magneto-Optical Rotation [Eq. (18b)]: Classes admitting of the effect
Voigt configuration (H_y)	x	xxyyy - yyyyy xxyzy - yyyzy xxzyy - yyzyy xxzzy - yyzyy	1, $\bar{1}$, m, 2, 2/m, 4, $\bar{4}$, 4/m, 3, $\bar{3}$, 6, $\bar{6}$, 6/m	xyyyy, xyyzy xyzyy, xyzzy	All classes
	y	xxzzy - yyzzy xxzxy - yyzxy xxxzy - yyxzy xxxxy - yyxxy	All classes	xyzzy, xyzxy xyxzy, xyxxy	1, $\bar{1}$, m, 2, 2/m, 4, $\bar{4}$, 4/m, 3, $\bar{3}$, 32, 3m, $\bar{3}$m, 6, $\bar{6}$, 6/m
	z	xxxxy - yyxxy xxxyy - yyxyy xxyxy - yyyxy xxyyy - yyyyy	1, $\bar{1}$, 3, $\bar{3}$, 32, 3m, $\bar{3}$m	xyxxy, xyxyy xyyxy, xyyyy	1, $\bar{1}$, 3, $\bar{3}$, 32, 3m, $\bar{3}$m

Faraday configuration (H_z)	x	xxyyz - yyyyz xxyzz - yyyzz xxzyz - yyzyz xxzzz - yyzzz	1, 1, m, 2, 2/m, 4, $\bar{4}$, 4/m, 3, $\bar{3}$, 6, $\bar{6}$, 6/m	xyyyz, xyyzz xyzyz, xyzzz	All classes
	y	xxzzz - yyzzz xxzxz - yyzxz xxxzz - yyxzz xxxxz - yyxxz	1, $\bar{1}$, m, 2, 2/m, 4, $\bar{4}$, 4/m, 3, $\bar{3}$, 32, 3m, $\bar{3}$m, 6, $\bar{6}$, 6/m	xyzzz, xyzxz xyxzz, xyxxz	All classes
	z	xxxxz - yyxxz xxxyz - yyxyz xxyxz - yyyxz xxyyz - yyyyz	All classes	xyxxz, xyxyz xyyxz, xyyyz	All classes

is of especial interest, since it can take place in isotropic bodies, where the axial tensor χ^{eeeem}_{ijklm} reduces its 243 elements to 60 nonzero ones, 6 of which are generally mutually independent. Besides frequency doubling, one has likewise the possibility of performing experimental studies of sum-frequency and difference-frequency processes at various configurations of the fields $\underline{E}(0)$ and $\underline{H}(0)$, in particular when the two fields are at right angles. As yet, there is a lack of reports on experimental attempts to deal with this new nonlinear magneto-optical process.

C. Third-Harmonic Generation

The theoretical work of Lax, Kolodziejczak, and others [62] has proved the feasibility of enhancement in THG due to interband transitions and resonance in the presence of a dc magnetic field. The relevant experiments have been performed by Patel et al. [63] in InSb single-crystal sample by using a Q-switched CO_2 laser and a magnetic field growing to 54 kOe. Phenomenologically, the effect is described in a first approximation by the following polarization at frequency 3ω resulting from Eq. (17):

$$P^e_i(3\omega) = \chi^{eeeem}_{ijkln}(3\omega)E_j(\omega)E_k(\omega)E_l(\omega)H_n(0) \tag{17b}$$

The above formula, moreover, describes THG in isotropic bodies with induced magnetic gyrotropy.

VI. EXPERIMENTAL PROSPECTS AND CONCLUSIONS

The preceding phenomenological treatment has permitted a concise discussion of the nature and observation conditions of a wide variety of new nonlinear magneto-electric-optical effects. Certain of these effects, like laser-induced magneto-optical rotation, SHG, and THG, are well known to have been detected and studied in semiconductor crystals [58,60,63], and everything points to their impending detection in molecular and macromolecular substances as well. To corroborate this statement, it suffices to invoke the inverse Faraday effect [39] detected in diamagnetic liquids and, in general, the recent rapid developments in laser technique. Ingenious methods of observation, supported by a high sensitivity of the measuring equipment and a judicious choice of substances and materials, will surely lead in the near future to detection of the other nonlinear magneto-optical effects discussed in this chapter.

The accretion of knowledge to be gained by investigations of these magneto-electro-optical effects in conjunction with other nonlinear processes, e.g., inverse Cotton-Mouton effect [48] and nonlinear light scattering in the presence of an electric and magnetic field [67], is obvious. In addition to the magneto-electric anisotropies of molecules and macromolecules, one will be in a position to determine nonlinear electron distortion processes which, hitherto, have been successfully calculated for some simple atoms and molecules only [68,69]. Despite the fact that general quantum mechanical theories of nonlinear magneto-electric polarizabilities [70] as well as discussions of the permutational properties of these tensors [71] are available, there is still a complete lack of papers claiming the evolvement of experimental methods and procedures. We know of but one report, concerning the observation of the influence of the square of a magnetic field on the electric permittivity of diamagnetic liquids [72].

The new magneto-electric-optical effects (particularly, nonlinear magnetic circular dichroism) can be detected soon and easily in macromolecular and colloidal solutions [40], especially liquid crystals. This statement is justified by the results achieved along the lines initiated by Jezewski [73] and Kast [74] showing that liquid crystals are highly sensitive not only to an electric field but to a magnetic field as well [75]. Quite recently, some more papers have appeared on the topics dealt with above [76-86].

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