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On new non-linear magneto-optical phenomena in crystals and liquids

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Abstract. Possibilities for the observation, in crystals and liquids, of new non-linear magneto-optical effects such as frequency mixing of laser beams and optical harmonics generation in the presence of a d.c. magnetic field, as well as non-linear magneto-optical birefringence and rotation at Faraday or Voigt configurations, are discussed in a phenomenological approach. The processes are described by axial non-linear magneto-electric susceptibility tensors $\chi_{ijkl}{}^{eeem}$ and $\chi_{ijkln}{}^{eeeem}$, whose non-zero and independent elements are calculated by group theoretical methods for all crystallographical classes.

1. Introduction

The introduction of laser techniques into laboratories has permitted an extension of classical magneto-optical studies on crystals [1–4] to non-linear optical phenomena in magnetized bodies [5–7]. In particular, equipment is now available for the study of d.c. magnetic field-induced second-harmonic generation of laser beams [6, 8, 9] as well as for the observation of large enhancements in higher harmonics due to resonance at high magnetic fields [10, 11], as in fact has been shown with regard to the third harmonic of CO_2 laser light in semiconductors [12]. Possibilities also exist for the observation of non-linear variations in magneto-optical rotation (Faraday effect) under the influence of laser light [13, 14], and of other magneto-optical cross effects [15].

It is the aim of this paper to draw attention to the experimental possibilities of detecting and studying various new non-linear magneto-optical effects to be expected in solids and liquids when acted on, in addition to a d.c. magnetic field, by d.c. electric fields or the oscillating electric field of laser light. The processes under consideration are described phenomenologically by axial tensors $\chi_{ijkl}{}^{eeem}$ and $\chi_{ijkln}{}^{eeeem}$ of non-linear magneto-electric susceptibilities, the non-zero and mutually independent tensor elements of which are calculated by standard methods of group theory [1, 3, 16, 17] for all crystallographical classes. Especial attention will be given to certain as yet unstudied optical properties of crystals, solids and fluids under the direct and simultaneous action of crossed externally applied electric and magnetic fields.

2. Non-linear magneto-optical polarizations

A light wave propagating in the direction $\mathbf{k}$ with electric vector $\mathbf{E}(\omega, \mathbf{k})$ and magnetic vector $\mathbf{H}(\omega, \mathbf{k})$ oscillating at frequency ω incident on a body gives rise in a first approximation to the linear electric dipole polarization:

$$P_i^{(1)}(\omega\,;\,\mathbf{k}) = \chi_{ij}{}^{ee}(\omega\,;\,\mathbf{k})E_j(\omega, \mathbf{k}) + \chi_{ij}{}^{em}(\omega, \mathbf{k})H_j(\omega, \mathbf{k}), \tag{1}$$

where the second-rank tensor $\chi_{ij}^{ee}(\omega, \mathbf{k})$ describes the linear electric susceptibility, whose dependence on the wave vector $\mathbf{k}$ and the frequency ω are referred to as space and frequency dispersion, respectively [2]. Likewise, χ_{ij}^{em} is the pseudo-tensor of linear electro-magnetic susceptibility [3].

2.1. *Second-order processes*

When the electromagnetic wave incident on the medium is of sufficiently high intensity, the linear relation (1) is no longer obeyed and induced polarizations of higher orders have to be taken into account. Quite generally, if two such waves, of frequencies ω_1 and ω_2 and wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ interact in the medium, the magneto-optical polarization of second-order induced at the frequency $\omega_3 = \omega_1 + \omega_2$ is:

$$P_i^{(2)}(\omega_3, \mathbf{k}_3) = \chi_{ijk}^{eem}(-\omega_3, \omega_1, \omega_2; -\mathbf{k}_3, \mathbf{k}_1, \mathbf{k}_2) E_j(\omega_1, \mathbf{k}_1) H_k(\omega_2, \mathbf{k}_2), \tag{2}$$

where the axial tensor of third rank χ_{ijk}^{eem} describes the magneto-electric susceptibility of the second order.

The polarization (2) of magneto-electric frequency mixing in a medium leads, in the particular case when $\omega_1 = \omega_2 = \omega$ and $\mathbf{k}_1 = \mathbf{k}_2 = \mathbf{k}$, to the magneto-electric contribution to second harmonic generation discussed by Jha [7]. In that of a static magnetic field $\omega_1 = \omega$, $\mathbf{k}_1 = \mathbf{k}$, $\omega_2 = \mathbf{k}_2 = 0$, the polarization (2) yields the following linear variation in electric permittivity:

$$\Delta\epsilon_{ij}^{(1)}(\omega, \mathbf{k}) = 4\pi \chi_{ijk}^{eem}(-\omega, \omega, 0; \mathbf{k}) H_k(0) \tag{3}$$

measured at the frequency ω as linear Faraday effect [5].

The pseudo-tensor χ_{ijk}^{eem} generally presents non-zero elements in bodies of all symmetries [3] (table 1).

2.2. *Third-order processes*

In the case of three distinct waves of frequencies ω_1, ω_2, ω_3 interacting in a medium, the non-linear magneto-electric polarization induced at the frequency $\omega_4 = \omega_1 + \omega_2 + \omega_3$ is (we restrict ourselves to the term linear in the magnetic vector):

$$P_i^{(3)}(\omega_4, \mathbf{k}_4) = \chi_{ijkl}^{eeem}(-\omega_4, \omega_1, \omega_2, \omega_3, \mathbf{k}_4) E_j(\omega_1, \mathbf{k}_1) E_k(\omega_2, \mathbf{k}_2) H_l(\omega_3, \mathbf{k}_3), \tag{4}$$

where the axial tensor of fourth rank χ_{ijkl}^{eeem} describes the non-linear magneto-electric susceptibility of the third order. The numbers of non-zero and independent tensor elements χ_{ijkl}^{eeem} are listed in table 1.

As a particular case of magneto-electric frequency mixing (4) we have, at $\omega_1 = \omega_2 = \omega$ and $\omega_3 = \mathbf{k}_3 = 0$, second harmonic generation in a d.c. magnetic field [8, 9]. At $\omega_1 = \omega$, $\mathbf{k}_1 = \mathbf{k}$ and $\omega_2 = \omega_3 = \mathbf{k}_2 = \mathbf{k}_3 = 0$, the polarization (4) leads to the following second-order variation of the electric permittivity tensor:

$$\Delta\epsilon_{ij}^{(2)}(\omega, \mathbf{k}) = 4\pi \chi_{ijkl}^{eeem}(-\omega, \omega, 0, 0, \mathbf{k}) E_k(0) H_l(0) \tag{5}$$

due to the simultaneous action of a d.c. electric field $E(0)$ and magnetic field $H(0)$.

Besides the magneto-electric contribution (4)—linear in H—we also have to deal with the following contribution, quadratic in H [6]:

$$P_i^{(3)}(\omega_4, \mathbf{k}_4) = \chi_{ijkl}^{eemm}(-\omega_4, \omega_1, \omega_2, \omega_3, \mathbf{k}_4) E_j(\omega_1, \mathbf{k}_1) H_k(\omega_2, \mathbf{k}_2) H_l(\omega_3, \mathbf{k}_3), \tag{6}$$

where the (polar) tensor χ_{ijkl}^{eemm} describes the non-linear susceptibility induced by the square of the magnetic field strength.

Table 1. The number of non-zero (N) and independent (I) elements of non-linear susceptibility axial tensors χ_{ijk}^{eem}, χ_{ijkl}^{eeem} and χ_{ijkln}^{eeeem}.

Class	$\chi_{i,j,k}^{eem}$		$\chi_{(ij)k}^{eem}$		$\chi_{i,j,k,l}^{eeem}$		$\chi_{(ij)k,l}^{eeem}$		$\chi_{(ijk)l}^{eeem}$		$\chi_{i,j,k,l,n}^{eeeem}$		$\chi_{(ij)k,l,n}^{eeeem}$		$\chi_{(ij)(kl)n}^{eeeem}$		$\chi_{(ijk)l,n}^{eeeem}$		$\chi_{(ijkl)n}^{eeeem}$	
	N	I	N	I	N	I	N	I	N	I	N	I	N	I	N	I	N	I	N	I
1(C1)	27	27	27	18	81	81	81	54	81	30	243	243	243	162	243	108	243	90	243	45
$\bar{1}$(Ci)	27	27	27	18	0	0	0	0	0	0	243	243	243	162	243	108	243	90	243	45
m(Cs)	13	13	13	8	40	40	40	26	40	14	121	121	121	80	121	52	121	44	121	21
2(C2)	13	13	13	8	41	41	41	28	41	16	121	121	121	80	121	52	121	44	121	21
2/m(C2h)	13	13	13	8	0	0	0	0	0	0	121	121	121	80	121	52	121	44	121	21
222(D2)	6	6	6	3	21	21	21	15	21	9	60	60	60	39	60	24	60	21	60	9
mm2(C2v)	6	6	6	3	20	20	20	13	20	7	60	60	60	39	60	24	60	21	60	9
mmm(D2h)	6	6	6	3	0	0	0	0	0	0	60	60	60	39	60	24	60	21	60	9
4(C4)	13	7	11	4	41	21	39	14	35	8	121	61	119	40	117	26	115	22	109	11
$\bar{4}$(S4)	13	7	11	4	40	20	40	14	40	8	121	61	119	40	117	26	115	22	109	11
4/m(C4h)	13	7	11	4	0	0	0	0	0	0	121	61	119	40	117	26	115	22	109	11
422(D4)	6	3	4	1	21	11	21	8	21	5	60	30	58	19	56	11	54	10	48	4
4mm(C4v)	6	3	4	1	20	10	18	6	14	3	60	30	58	19	56	11	54	10	48	4
$\bar{4}$2m(D2d)	6	3	4	1	20	10	20	7	20	4	60	30	58	19	56	11	54	10	48	4
4/mmm(D4h)	6	3	4	1	0	0	0	0	0	0	60	30	58	19	56	11	54	10	48	4
3(C3)	21	9	19	6	73	27	71	18	67	10	233	81	231	54	229	36	227	30	213	15
$\bar{3}$(S6)	21	9	19	6	0	0	0	0	0	0	233	81	231	54	229	36	227	30	213	15
32(D3)	10	4	8	2	37	14	37	10	37	6	116	40	114	26	112	16	110	14	96	6
3m(C3v)	10	4	8	2	36	13	34	8	30	4	116	40	114	26	112	16	110	14	96	6
$\bar{3}$m(D3d)	10	4	8	2	0	0	0	0	0	0	116	40	114	26	112	16	110	14	96	6
6(C6)	13	7	11	4	41	19	39	12	35	6	121	51	119	32	117	20	115	16	101	7
$\bar{6}$(C3h)	13	7	11	4	32	8	32	6	32	4	121	51	119	32	117	20	115	16	101	7
6/m(C6h)	13	7	11	4	0	0	0	0	0	0	121	51	119	32	117	20	115	16	101	7
622(D6)	6	3	4	1	21	10	21	7	21	4	60	25	58	15	56	8	54	7	40	2
6mm(C6v)	6	3	4	1	20	9	18	5	14	2	60	25	58	15	56	8	54	7	40	2
6m2(D3h)	6	3	4	1	16	4	16	3	16	2	60	25	58	15	56	8	54	7	40	2
6/mmm(D6h)	6	3	4	1	0	0	0	0	0	0	60	25	58	15	56	8	54	7	40	2
23(T)	6	2	6	1	21	7	21	5	21	3	60	20	60	13	60	8	60	7	60	3
m3(Th)	6	2	6	1	0	0	0	0	0	0	60	20	60	13	60	8	60	7	60	3
432(O)	6	1	0	0	21	4	21	3	21	2	60	10	54	6	48	3	42	3	24	1
$\bar{4}$3m(T)	6	1	0	0	18	3	18	2	18	1	60	10	54	6	48	3	42	3	24	1
m3m(Oh)	6	1	0	0	0	0	0	0	0	0	60	10	54	6	48	3	42	3	24	1
Y	6	1	0	0	21	3	21	2	21	1	60	6	54	3	48	1	42	1	0	0
Yh	6	1	0	0	0	0	0	0	0	0	60	6	54	3	48	1	42	1	0	0
K	6	1	0	0	21	3	21	2	21	1	60	6	54	3	48	1	42	1	0	0
Kh	6	1	0	0	0	0	0	0	0	0	60	6	54	3	48	1	42	1	0	0

The magneto-electric polarization (6) plays an insignificant role in processes of frequency mixing and harmonics generation but in particular causes the following quadratic change in the tensor of electric permittivity:

$$\Delta\epsilon_{ij}^{(2)}(\omega, \mathbf{k}) = 4\pi\chi_{ijkl}{}^{eemm}(-\omega,\omega,0,0,\mathbf{k})H_k(0)H_l(0), \tag{7}$$

measured as Cotton–Mouton effect, and magnetostriction.

2.3. *Fourth-order processes*

In various cases polarizations of higher orders have to be considered, in particular the following fourth-order magneto-electric polarization induced at the frequency $\omega_5 = \omega_1 + \omega_2 + \omega_3 + \omega_4$ (for brevity, we omit the wave vectors):

$$P_i^{(4)}(\omega_5) = \chi_{ijkln}{}^{eeeem}(-\omega_5,\omega_1,\omega_2,\omega_3,\omega_4)E_j(\omega_1)E_k(\omega_2)E_l(\omega_3)H_n(\omega_4), \tag{8}$$

where the axial tensor of fifth rank $\chi_{ijkln}{}^{eeeem}$ describes a non-linear magneto-electric susceptibility of the fourth order generally present in all bodies (table 1).

In particular, at $\omega_1 = \omega_2 = \omega_3 = \omega$ and $\omega_4 = 0$, the polarization (8) describes the process of third harmonic generation in a d.c. magnetic field studied in semi-conductors [10–12]. But if $\omega_3 = \omega_4 = 0$, it describes frequency mixing or (at $\omega_1 = \omega_2$) second harmonic generation in crossed d.c. electric and magnetic fields [18]. Particularly interesting is the case when $\omega_1 = \omega$, $\omega_2 = -\omega_3 = \omega_L$ and $\omega_4 = 0$, since now the polarization (8) leads to a third-order change in the electric permittivity tensor:

$$\Delta\epsilon_{ij}^{(3)}(\omega) = 4\pi\chi_{ijkln}{}^{eeeem}(-\omega,\omega,\omega_L,-\omega_L,0)E_k(\omega_L)E_l(-\omega_L)H_n(0). \tag{9}$$

On comparison with equation (3), the variation given in equation (9) is seen to describe the influence of strong laser light of intensity $E_k(\omega_L)E_l(-\omega_L)$ on the linear Faraday effect [13]. Especially, at $\omega_L = 0$, (9) describes the non-linear change in Faraday effect due to a d.c. electric field $E(0)$.

3. Conditions for the observation of new magneto-optical effects

Whether or not the new magneto-optical phenomena defined by equations (4)–(9) can be observed experimentally depends, on the one hand, on the experimental facilities available and, on the other, on a judicious choice of crystalline and liquid materials (in particular, on the type of their crystal symmetry).

3.1. *Processes involving mixing and generation of harmonics*

Table 1 which, beside the tensor $\chi_{ijk}{}^{eem}$, gives the non-zero and independent elements of the new axial tensors $\chi_{ijkl}{}^{eeem}$ and $\chi_{ijkln}{}^{eeeem}$, enables us to specify those symmetry classes where magneto-optical processes of laser frequency mixing and second (or third) harmonic generation can be predicted to occur. By analogy to equation (4), we have the non-linear magneto-optical polarization:

$$P_i^{(3)}(\omega_3, \mathbf{k}_3) = \chi_{ijkl}{}^{eeem}(-\omega_3, \omega_1, \omega_2, 0; \mathbf{k}_3)E_j(\omega_1, \mathbf{k}_1)E_k(\omega_2, \mathbf{k}_2)H_l(0), \qquad (10)$$

stating that, as a result of magnetization, bodies will exhibit processes of frequency mixing and harmonics generation in the classes 422(D_4), 622(D_6), 432(0), Y andK forbidden in the electric dipole approximation in the absence of a d.c. magnetic field. In the remaining classes without a centre of symmetry naturally exhibiting electric dipole second harmonic generation, the application of a d.c. magnetic field $H(0)$ will enhance the second harmonic intensity.

Higher-order optical processes, induced by a d.c. magnetic field, are described by the following polarization at frequency $\omega_4 = \omega_1 + \omega_2 + \omega_3$:

$$P_i^{(4)}(\omega_4) = \chi_{ijkln}{}^{eeeem}(-\omega_4, \omega_1, \omega_2, \omega_3, 0)E_j(\omega_1)E_k(\omega_2)E_l(\omega_3)H_n(0) \qquad (11)$$

generally presented by all crystallographical classes.

3.2. *Non-linear magneto-optical birefringence and rotations*

If stricter conditions of symmetricity or anti-symmetricity are imposed on the indices i,j,k,l,n of the axial tensors $\chi_{ijk}{}^{eem}$, $\chi_{ijkl}{}^{eeem}$, $\chi_{ijkln}{}^{eeeem}$, the number of their non-zero and mutually independent elements undergoes a reduction, as shown by table 1. Quite generally, each of these tensors is separable into parts symmetric and anti-symmetric with respect to the pair of indices i, j. The symmetric parts (table 1):

$$\chi_{(ij)k}{}^{eem} = \chi_{(ji)k}{}^{eem}, \quad \chi_{(ij)kl}{}^{eeem} = \chi_{(ji)kl}{}^{eeem}, \quad \chi_{(ij)kln}{}^{eeeem} = \chi_{(ji)kln}{}^{eeeem} \qquad (12\,a)$$

contribute to the diagonal elements of the changes in electric permittivity tensor which define magneto-optical birefringence effects, whereas the antisymmetric parts (table 2):

$$\chi_{[ij]k}{}^{eem} = -\chi_{[ji]k}{}^{eem}, \quad \chi_{[ij]kl}{}^{eeem} = -\chi_{[ji]kl}{}^{eeem}, \quad \chi_{[ij]kln}{}^{eeeem} = -\chi_{[ji]kln}{}^{eeeem}, \qquad (12\,b)$$

contribute to the non-diagonal elements of the changes in electric permittivity tensor defining magneto-optical rotation effects. In our analysis of the tensors (12) by group theory methods [3, 16, 17] we took into consideration their dependence on space dispersion, determined by appropriate multipole electric and magnetic contributions [6].

Table 2. Non-zero and independent elements of the axial tensors $\chi^{eem}_{[ij]k}$, $\chi^{eeem}_{[ij]k,l}$ and $\chi^{eeeem}_{[ij]k,l,n}$ for all crystallographical classes. The tensor elements are denoted by their subscripts x, y, z only. N signifies the number of non-zero elements, I that of independent elements. In order to reduce space, elements shared by various classes have been assembled under one capital letter.

Class	$\chi^{eem}_{[ij]k}$			$\chi^{eeem}_{[ij]k,l}$			$\chi^{eeeem}_{[ij]k,l,n}$		
	N	I	Elements	N	I	Elements	N	I	Elements
1(C_1)	18	9	$A_1 \equiv$ xyy = −yxy, yxx = −xyx, $B_1 \equiv$ zxx = −xzx, zyy = −yzy, $D_1 \equiv$ xzz = −zxz, yzz = −zyz, $E_1 \equiv$ xyz = −yxz, xzy = −zxy, yzx = −zyx,	54	27	$A_2 \equiv$ xyyx = −yxyx, yxxy = −xyxy, xzzx = −zxzx, xzxz = −zxxz, yzzy = −zyzy, yzyz = −zyyz, $B_2 \equiv$ xyxx = −yxxx, yxyy = −xyyy. xzzy = −zxzy, yzzx = −zyzx, xyzz = −yxzz, xzyz = −zxyz, yzxz = −ɛyxz, $D_2 \equiv$ xzxx = −zxxx, xzzz = −zxzz, xyyz = −yxyz, xyzy = −yxzy, xzyy = −zxyy. yzyx = −zyyx, yzxy = −zyxy, $E_2 \equiv$ yzyy = −zyyy, yzzz = −zyzz, xyxz = −yxxz, xyzx = −yxzx, xzxy = −zxxy, xzyx = −zxyx, yzxx = −zyxx,	162	81	$A_3 \equiv$ xzxxx = −zxxxx, yzyyy = −zyyyy, $B_3 \equiv$ xzxzz = −zxxzz, xzzxz = −zxzxz, xzzzx = −zxzzx, yzzzy = −zyzzy, yzyzz = −zyyzz, yzzyz = −zyzyz, $D_3 \equiv$ xyxxz = −yxxxz, xzxxy = −zxxxy, xyxzx = −yxxzx, xzxyx = −zxxyx, xyzxx = −yxzxx, xzyxx = −zxyxx, zyxxx = −yzxxx, yxyyz = −xyyyz, yzyyx = −zyyyx, yxyzy = −xyyzy, yzyxy = −zyyxy, yxzyy = −xyzyy, yzxyy = −zyxyy, xzyyy = −zxyyy, zxzzy = −xzzzy, zyzzx = −yzzzx, zxzyz = −xzzyz, zyzxz = −yzzxz, zxyzz = −xzyzz, zyxzz = −yzxzz, xyzzz = −yxzzz, $E_3 \equiv$ xyxyz = −yxxyz, xyzxy = −yxzxy, xyxzy = −yxxzy, xyzyx = −yxzyx, xyyzx = −yxyzx, xzxyy = −zxxyy, xyyxz = −yxyxz, xzyxy = −zxyxy, yzxxy = −zyxxy, xzyyx = −zxyyx, yzxyx = −zyxyx, yzyxx = −zyyxx, $F_3 \equiv$ xyxxx = −yxxxx, xyyyy = −yxyyy, xzzzz = −zxzzz, yzzzz = −zyzzz, xyxyx = −yxxyx, xyxxy = −yxxxy. xyyxx = −yxyxx, xyxyy = −yxxyy, xyyxy = −yxyxy, xyyyx = −yxyyx, xzxzx = −zxxzx, xzxxz = −zxxxz, xzzxx = −zxzxx, yzyzy = −zyyzy, yzyyz = −zyyyz, yzzyy = −zyzyy, xzxzy = −zxxzy, xyxzz = −yxxzz, xzxyz = −zxxyz, xyzxz = −yxzxz, xzzyz = −zxzyz, xyzzx = −yxzzx, xzzxy = −zxzxy, zyxxz = −yzxxz, xzyxz = −zxyxz, zyxzx = −yzxzx, xzyzx = −zxyzx, zyzxx = −yzzxx, yzyzx = −zyyzx, yxyzz = −xyyzz, yzyxz = −zyyxz, yxzyz = −xyzyz, yzzxy = −zyzxy, yxzzy = −xyzzy, yzzyx = −zyzyx, zxyyz = −xzyyz, yzxyz = −zyxyz, zxyzy = −xzyzy, yzxzy = −zyxzy, zxzyy = −xzzyy,
$\bar{1}$(Ci)	18	9	A_1, B_1, D_1 and E_1	0	0		162	81	A_3, B_3, D_5, E_3 and F_3
2(C2)	10	5	B_1 and E_1	26	13	A_2 and B_2	82	41	A_3, B_3, D_3 and E_3
m(Cs)	10	5	B_1 and E_1	28	14	D_2 and E_2	82	41	A_3, B_3, D_3 and E_3
2/m(C2h)	10	5	B_1 and E_1	0	0		82	41	A_3, B_3, D_3 and E_3
222(D2)	6	3	E_1	12	6	A_2	42	21	D_3
mm2(C2v)	6	3	E_1	14	7	B_2	42	21	D_3
mmm(D2h)	6	3	E_1	0	0		42	21	D_3

[*continued on next page*

Table 2—*continued*

Class	$\chi^{eem}_{[ij]k}$			$\chi^{eeem}_{[ij]k,l}$			$\chi^{eeeem}_{[ij]k,l,n}$		
	N	I	Elements	N	I	Elements	N	I	Elements
4(C4)	10	3	$F_1 \equiv zxx = -xzx =$ $zyy = -yzy,$ $G_1 \equiv xyz = -yxz,$ $xzy = -zxy =$ $zyx = -yzx,$	26	7	$F_2 \equiv xyyx = -yxyx = yxxy = -xyxy,$ $xzzx = -zxzx = yzzy = -zyzy,$ $xzxz = -zxxz = yzyz = -zyyz,$ $G_2 \equiv xyxx = -yxxx = xyyy = -yxyy,$ $H_2 \equiv xyzz = -yxzz,$ $J_2 \equiv xzzy = -zxzy = zyzx = -yzzx,$ $xzyz = -zxyz = zyxz = -yzxz,$	82	21	$G_3 \equiv xzxxx = -zxxxx = yzyyy = -zyyyy,$ H_3 $xzxzz = -zxxzz = yzyzz = -zyyzz,$ $xzzxz = -zxzxz = yzzyz = -zyzyz,$ $xzzzx = -zxzzx = yzzzy = -zyzzy,$ $J_3 \equiv xyxxz = -yxxxz = xyyyz = -yxyyz,$ $xyxzx = -yxxzx = xyyzy = -yxyzy,$ $xyzxx = -yxzxx = xyzyy = -yxzyy,$ $xzxxy = -zxxxy = zyyyx = -yzyyx,$ $xzxyx = -zxxyx = zyyxy = -yzyxy,$ $xzyxx = -zxyxx = zyxyy = -yzxyy,$ $zyxxx = -yzxxx = xzyyy = -zxyyy,$ $L_3 \equiv zxzzy = -xzzzy = yzzzx = -zyzzx,$ $zxzyz = -xzzyz = yzzxz = -zyzxz,$ $zxyzz = -xzyzz = yzxzz = -zyxzz,$ $xyzzz = -yxzzz,$ $M_3 \equiv xyxyz = -yxxyz = yxyxz = -xyyxz,$ $xyxzy = -yxxzy = yxyzx = -xyyzx,$ $xyzxy = -yxzxy = yxzyx = -xyzyx,$ $xzyxy = -zxyxy = yzxyx = -zyxyx,$ $xzxyy = -zxxyy = yzyxx = -zyyxx,$ $xzyyx = -zxyyx = yzxxy = -zyxxy,$
4/m(C4h)	10	3	F_1 and G_1	0	0		82	21	G_3, H_3, J_3, L_3 and M_3
422(D4)	6	2	G_1	12	3	F_2	42	11	J_3 and L_3
4mm(C4v)	6	2	G_1	14	4	G_2, H_2 and J_2	42	11	J_3 and L_3
$\bar{4}$(S4)	10	3	F_1 and G_1	24	6	$F_2^* \equiv xyyx = -yxyx = xyxy = -yxxy,$ $xzzx = -zxzx = zyzy = -yzzy,$ $xzxz = -zxxz = zyyz = -yzyz,$ $J_2^* \equiv xzzy = -zxzy = yzzx = -zyzx,$ $xzyz = -zxyz = yzxz = -zyxz,$ $G_2^* \equiv xyxx = -yxxx = yxyy = -xyyy$	82	21	G_3, H_3, J_3, L_3 and M_3
$\bar{4}$2m(D2d)	6	2	G_1	12	3	F_2^*	42	11	J_3 and L_3
4/mmm(D4h)	6	2	G_1	0	0		42	11	J_3 and L_3

[*continued on next page*

Table 2—*continued*

Class	$\chi^{eem}_{[ij]k}$			$\chi^{eeem}_{[ij]k,l}$			$\chi^{eeeem}_{[ij]k,l,n}$		
	N	I	Elements	N	I	Elements	N	I	Elements
$3(C_3)$	10	3	F_1 and G_1	42	9	F_2, G_2, H_2, J_2 and $L_2 \equiv xzxx = -zxxx = zyyx = -yzyx = zyxy = -yzxy =$ $zxyy = -xzyy$, $M_2 \equiv yzyy = -zyyy = zxxy = -xzxy = zxyx = -xzyx =$ $zyxx = -yzxx$,	146	27	H_3, L_3, M_3 and $P_3 \equiv G_3 = xzxyy + xzyxy + xzyyx$, $Q_3 \equiv xzxxy = -zxxxy = -yzyyx = zyyyx =$ $= -(xzxyx + xzyxx + yzxxx)$, $xzxyx = -zxxyx = zyyxy = -yzyxy$, $xyxxz = -yxxxz = xyyyz = -yxyyz$, $xyxzx = -yxxzx = xyyzy = -yxyzy$, $xyzxx = -yxzxx = xyzyy = -yxzyy$, $zyxxx = -yzxxx = xzyyy = -zxyyy$, $xzyxx = -zxyxx = zyxyy = -yzxyy$, $R_3 \equiv xzxxz = -zxxxz = zxyyz = -xzyyz =$ $zyyxz = -yzyxz = zyxyz = -yzxyz$, $xzxzx = -zxxzx = zxyzy = -xzyzy =$ $zyyzx = -yzyzx = zyxzy = -yzxzy$, $xzzxx = -zxzxx = zxzyy = -xzzyy =$ $zyzxy = -yzzxy = zyzyx = -yzzyx$, $S_3 \equiv xyxxy = -yxxxy = xyyxx = -yxyxx =$ $xyxyx = -yxxyx = yxyyy = -xyyyy$, $U_3 \equiv yzyyz = -zyyyz = zyxxz = -yzxxz =$ $zxxyz = -xzxyz = zxyxz = -xzyxz$, $yzyzy = -zyyzy = zyxzx = -yzxzx =$ $zxxzy = -xzxzy = zxyzx = -xzyzx$, $yzzyy = -zyzyy = zyzxx = -yzzxx =$ $zxzyx = -xzzyx = zxzxy = -xzzxy$, $yxxxx = -xyxxx = xyyyx = -yxyyx =$ $xyxyy = -yxxyy = xyyxy = -yxyxy$,
$\bar{3}(S6)$	10	3	F_1 and G_1	0	0		146	27	H_3, L_3, M_3, P_3, Q_3, R_3, S_3 and U_3
32(D3)	6	2	G_1	20	4	F_2 and M_2	74	14	L_3, Q_3, R_3 and S_3
3m(C3v)	6	2	G_1	22	5	G_2, H_2, J_2 and L_2	74	14	L_3, Q_3, R_3 and S_3
$\bar{3}$m(D3d)	6	2	G_1	0	0		74	14	L_3, Q_3, R_3 and S_3
6(C6)	10	3	F_1 and G_1	26	7	F_2, G_2, H_2 and J_2	82	19	H_3, L_3, M_3, P_3 and Q_3
$\bar{6}$(C3h)	10	3	F_1 and G_1	16	2	L_2 and M_2	82	19	H_3, L_3, M_3, P_3 and Q_3
6/m(C6h)	10	3	F_1 and G_1	0	0		82	19	H_3, L_3, M_3, P_3 and Q_3
622(D6)	6	2	G_1	12	3	F_2	42	10	L_3 and Q_3
6mm(C6v)	6	2	G_1	14	4	G_2, H_2 and J_2	42	10	L_3 and Q_3

[continued on next page

Table 2—*continued*

Class	$\chi^{eem}_{[ij]k}$			$\chi^{eeem}_{[ij]k,l}$			$\chi^{eeeem}_{[ij]k,l,n}$		
	N	I	Elements	N	I	Elements	N	I	Elements
$\bar{6}$m2(D3h)	6	2	G_1	8	1	M_2	42	10	L_3 and Q_3
6/mmm(D6h)	6	2	G_1	0	0		42	10	L_3 and Q_3
23(T)	6	1	$H_1 \equiv xyz = -yxz =$ $zxy = -xzy =$ $yzx = -zyx$	12	2	$P_2 \equiv xyyx = -yxyx = zxxz = -xzxz = yzzy = -zyzy,$ $Q_2 \equiv yxxy = -xyxy = xzzx = -zxzx = zyyz = -yzyz,$	42	7	$xzxyx = -zxxyx = yxyzy = -xyyzy = zyzxz = -yzzxz,$ $xzxxy = -zxxxy = yxyyz = -xyyyz = zyzzx = -yzzzx,$ $xzyxx = -zxyxx = yxzyy = -xyzyy = zyxzz = -yzxzz,$ $xyzxx = -yxzxx = yzxyy = -zyxyy = zxyzz = -xzyzz,$ $xyxzx = -yxxzx = yzyxy = -zyyxy = zxzyz = -xzzyz,$ $xyxxz = -yxxxz = yzyyx = -zyyyx = zxzzy = -xzzzy,$ $yzxxx = -zyxxx = zxyyy = -xzyyy = xyzzz = -yxzzz,$
m3(Th)	6	1	H_1	0	0		42	7	The same as in class 23(T)
432(O)	6	1	H_1	12	1	$P_2 = Q_2$	42	4	$V_3 \equiv xzxyx = -zxxyx = yxyzy = -xyyzy = zyzxz = -yzzxz =$ $yxxzx = -xyxzx = zyyxy = -yzyxy = xzzyz = -zxzyz,$ $xzxxy = -zxxxy = yxyyz = -xyyyz = zyzzx = -yzzzx =$ $yxxxz = -xyxxz = zyyyx = -yzyyx = xzzzy = -zxzzy,$ $xzyxx = -zxyxx = yxzyy = -xyzyy = zyxzz = -yzxzz =$ $yxzxx = -xyzxx = zyxyy = -yzxyy = xzyzz = -zxyzz,$ $W_3 \equiv yzxxx = -zyxxx = zxyyy = -xzyyy = xyzzz = -yxzzz,$
$\bar{4}$3m(Td)	6	1	H_1	12	1	$P_2 = -Q_2$	42	4	V_3 and W_3
m3m(Oh)	6	1	H_1	0	0		42	4	V_3 and W_3
Y and K	6	1	H_1	12	1	$P_2 = Q_2$	42	3	V_3 and $W_3 \equiv -(xzxyx + xzxxy + xzyxx)$
Yh and Kh	6	1	H_1	0	0		42	3	V_3 and W_3 $-(xzxyx + xzxxy + xzyxx)$

At analysing light (frequency ω_A) propagating along Z, the difference $\Delta\epsilon_{xx}(\omega_A) - \Delta\epsilon_{yy}(\omega_A)$ defines optical birefringence, whereas the difference $\Delta\epsilon_{xy}(\omega_A) - \Delta\epsilon_{yx}(\omega_A)$ defines optical rotation.

In second-order approximation, we have by (7) the magneto-optical birefringence as:

$$\Delta\epsilon_{xx}^{(2)}(\omega_A) - \Delta\epsilon_{yy}^{(2)}(\omega_A) = 4\pi \{\chi_{xxij}{}^{eeem}(-\omega_A, \omega_A, 0, 0; \mathbf{k}_A) - \chi_{yyij}{}^{eeem}(-\omega_A, \omega_A, 0, 0; \mathbf{k}_A)\} E_i(0) H_j(0) \tag{13}$$

and magneto-optical rotation in the form:

$$\Delta\epsilon_{xy}^{(2)}(\omega_A) - \Delta\epsilon_{yx}^{(2)}(\omega_A) = 8\pi \chi_{xyij}{}^{eeem}(-\omega_A, \omega_A, 0, 0; \mathbf{k}_A) E_i(0) H_j(0). \tag{14}$$

When studying observation conditions for the effects (13) and (14), the following two limiting situations have to be considered: (i) Voigt configuration (the analysing beam propagates perpendicularly to the d.c. magnetic field); and (ii) Faraday configuration (the analysing beam propagates along the d.c. magnetic field direction, i.e. along the Z-axis). In table 3 are listed the theoretically predicted situations for observing the new second-order magneto-optical effects (13) and (14) defining the changes in optical properties of bodies induced by the simultaneous action of d.c. electric and magnetic fields.

Table 3. Predicted experimental situations for the observation of second-order magneto-optical birefringence and rotation.

The analysing light beam propagates along Z at:	Direction of electric field action	Magneto-optical birefringence		Magneto-optical rotation	
		Relevant tensor elements $\chi^{eeem}_{(ij)kl}$	Crystallographical classes admitting of the effect	Relevant tensor elements $\chi^{eeem}_{[ij]kl}$	Crystallographical classes admitting of the effect
Voigt configuration (H_y)	x	$xxxy - yyxy$	1, 2, mm2, 4, $\bar{4}$, 4mm, 3, 3m, 6, 6mm	$xyxy = -yxxy$	$\underline{1}$, 2, 222, 4, $\bar{4}$, 422, $\bar{4}$2m, 3, $\underline{32}$, 6, 622, 23, 432, $\bar{4}$3m, Y, K
	y	$xxyy - yyyy$	$\underline{1}$, 2, 222, 4, $\bar{4}$, 422, $\bar{4}$2m, 3, $\underline{32}$, 6, 622, 23, 432, $\bar{4}$3m, 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	$xxzz - yyzz$	$\underline{1}$, 2, 222, $\bar{4}$, $\bar{4}$2m $\bar{4}$3m, 23	$xyzz = -yxzz$	1, 2, mm2, 4, 4mm, 3, 3m, 6, 6mm

By (9), we derive the following third-order magneto-optical birefringence:

$$\Delta\epsilon_{xx}^{(3)}(\omega_A) - \Delta\epsilon_{yy}^{(3)}(\omega_A) = 8\pi \{\chi_{xxijk}{}^{eeeem}(-\omega_A, \omega_A, \omega_L, -\omega_L, 0; \mathbf{k}_A) - \chi_{yyijk}{}^{eeeem}(-\omega_A, \omega_A, \omega_L, -\omega_L, 0, \mathbf{k}_A)\} I_{ij} H_k(0), \tag{15}$$

and magneto-optical rotation:

$$\Delta\epsilon_{xy}^{(3)}(\omega_A) - \Delta\epsilon_{yx}^{(3)}(\omega_A) = 16\pi \chi_{xyijk}{}^{eeeem}(-\omega_A, \omega_A, \omega_L, -\omega_L, 0, \mathbf{k}_A) I_{ij} H_k(0), \tag{16}$$

where the second-rank tensor

$$I_{ij} = E_i(\omega_L) E_j(-\omega_L)/2$$

is that of the light intensity causing optical non-linearity in the medium.

The theoretically predicted possibilities for the observation of non-linear magneto-optical effects induced by intense light are listed in table 4. Obviously, when determining observation conditions for the effects (13)–(16), necessary conditions have to be established which are by no means sufficient in all cases (thus, e.g., one has to take into consideration the propagation direction of the analysing beam with respect to the optical axis of the crystal, the state of polarization—line, circular or elliptical—of the analysing beam, and so forth). Of late, Kubota [14] has observed light-intensity dependent magnetic rotation at Faraday's configuration in semiconducting crystals (ZnS, CdS). It is felt that the new magneto-optical effects discussed here can also be observed in other crystals [19], as well as in isotropic bodies, especially in regions of absorption [13, 15, 20], and in ferromagnetic metals [21].

Table 4. Predicted experimental situations for the observation of third-order magneto-optical birefringence and rotation.

The analysing light beam propagates along Z at:	Propagation direction of inducing laser light	Magneto-optical birefringence		Magneto-optical rotation	
		Relevant tensor elements $\chi^{eeeem}_{(ij)kln}$	Classes admitting of the effect	Relevant tensor elements $\chi^{eeeem}_{[ij]kln}$	Classes admitting of the effect
Voigt configuration (H_y)	x	$xxyyy-yyyyy$ $xxyzy-yyyzy$ $xxzyy-yyzyy$ $xxzzy-yyzyy$	$\underline{1}$, $\bar{1}$, m, 2. $\underline{2}$/m, $\underline{4}$, $\bar{4}$, 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	$xyzzy$, $xyzxy$ $xyxzv$, $xyxxy$	$\underline{1}$, $\bar{1}$, m, $\underline{2}$, 2/m, 4, $\underline{4}$, 4/m, $\underline{3}$, $\bar{3}$, 32, 3m, $\bar{3}$m, 6, $\bar{6}$, 6/m
	z	$xxxxy-yyxxy$ $xxxyy-yyxyy$ $xxyxy-yyyxy$ $xxyyy-yyyyy$	$\underline{1}$, $\bar{1}$, 3, $\bar{3}$, 32, 3m, $\bar{3}$m	$xyxxy$, $xyxyy$ $xyyxy$, $xyyyy$	$\underline{1}$, $\bar{1}$, 3, $\bar{3}$, 32, 3m, $\bar{3}$m
Faraday configuration (Hz)	x	$xxyyz-yyyyz$ $xxyzz-yyyzz$ $xxzyz-yyzyz$ $xxzzz-yyzzz$	$\underline{1}$, $\bar{1}$, m, 2, $\underline{2}$/m, $\underline{4}$, $\bar{4}$, 4/m, 3, $\bar{3}$, 6, $\bar{6}$, 6/m	$xyyyz$, $xyyzz$ $xyzyz$, $xyzzz$	All classes
	y	$xxzzz-yyzzz$ $xxzxz-yyzxz$ $xxxzz-yyxzz$ $xxxxz-yyxxz$	$\underline{1}$, $\bar{1}$, m, $\underline{2}$, 2/m, 4, $\underline{4}$, 4/m, $\underline{3}$ $\bar{3}$, 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

4. Conclusions

The preceding phenomenological discussion shows that the second-order magneto-optical birefringence (13) depends largely on spatial dispersion, whereas magneto-optical rotation can be induced even in the classes 4mm, 3m, 6mm, $\bar{4}$3m and Y comprising crystals without natural optical activity. Laser light intensity-dependent magneto-optical birefringence and rotation can occur in almost all of the crystallographical classes as well as in isotropic bodies, at both Faraday and Voigt configurations. The complete analysis of the problem involves the solving of Fresnel's equation for refractive indices providing the basis of non-linear crystallo-magneto-optics. Also, investigation can extend to processes of frequency mixing as well as second and third harmonic generation in the presence of a d.c. magnetic field.

Les possibilités de détection et d'observation dans les solides et les fluides, de certains nouveaux effets non linéaires magnéto-optiques (brassage de fréquences des faisceaux de lasers et génération des harmoniques optiques en présence d'un champ magnétique statique, gyration non linéaire magnéto-optique en configuration de Faraday et de Voigt) sont prédites et discutées phénoménologiquement. Les éléments non-nuls et indépendants des tenseurs axiaux χ_{ijkl}^{eeem} et χ_{ijkln}^{eeeem} décrivant ces processus sont calculés par les méthodes de la théorie des groupes pour toutes les classes cristallographiques.

Es werden phänomenologisch behandelt Möglichkeiten für die Beobachtung neuer nichtlinearer magneto-optischer Effekte in Kristallen und Flüssigkeiten, wie Frequenzmischung von Laser Bündeln und Erzeugung optischer Oberwellen in Anwesenheit eines konstanten magnetischen Feldes, sowie nichtlineare magneto-optischer Doppelbrechung und Drehung bei Faraday oder Voigt Konfigurationen. Die Prozesse werden durch magneto-elektrische Suszeptibilitäts-Tensoren χ_{ijkl}^{eeem} und χ_{ijkln}^{eeeem}, deren nichtverschwindende und unabhängige Elemente für alle kristallographische Klassen mittels gruppentheoretischer Methoden berechnet werden, beschrieben.

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