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Selection Rules for Circularly Polarized Waves in Nonlinear Optics

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The symmetry properties of nonlinear optical susceptibilities in the electric dipole approximation for collinear circularly or elliptically polarized light waves have been analyzed on the basis of group-theoretical considerations. Selection rules are obtained for the nonlinear interaction of arbitrary order along any symmetry axis of the 32 crystallographic groups and the three-dimensional rotation group.

I. INTRODUCTION

It is well known that nonlinear optical interactions in crystalline substances are dependent on both the symmetry properties of the medium and the state of polarization of the interacting radiation. With respect to the latter, the primary research emphasis has been in considering the radiation to be linearly polarized. In the last few years, however, there has been an increasing interest in the use of circularly polarized waves in nonlinear processes. First, the anticipated selection rules involving circularly polarized radiation for both second- and third-harmonic generation have been substantiated.[1–4] For example, a circularly polarized laser wave produces a second harmonic with opposite sense of circular polarization along a threefold axis, and no third harmonic can be produced in an isotropic medium using circularly polarized radiation. In addition, harmonic generation employing circularly polarized laser radiation has been recently correlated with the unique symmetry properties of a liquid-crystal medium.[5] Second, the question of conservation of angular momentum of nonlinear interactions of circularly polarized waves has been investigated.[6] Third, circular birefringence may be employed in phase matching a nonlinear optical interaction,[1,7,8] and this technique has been applied to difference-frequency generation in the far infrared.[9] Fourth, the use of circularly polarized waves in third-harmonic generation has resulted in a new measurement of the time duration of picosecond optical pulses.[10]

In Table I a summary is presented of experimental results for the nonlinear interactions of circularly polarized radiation. The media employed, the corresponding symmetry group, and the axis of symmetry in the direction of propagation are indicated. All these results are in agreement with the theoretical predictions discussed in the various references cited. Previous theoretical work in accounting for the behavior of nonlinear interactions of circularly polarized waves has been based primarily upon explicit calculations from the known forms of the second- and third-order nonlinear susceptibilities or of the crystal field for particular point groups. These results have been obtained to third order in the nonlinearity.[1,2] The connection between these selection rules and the conservation of angular momentum have been discussed in detail by Bloembergen.[2,6]

In this paper, a general method of obtaining the selection rules for the nonlinear interactions of collinear circularly polarized waves has been developed using group-theoretical considerations. It has similarly been applied to collinear elliptically polarized waves. The method is described in Sec. II and applied to all 32 point groups and the three-dimensional rotation group and it is applicable to any order in the nonlinearity. Furthermore, this treatment leads to the prediction of the existence of recursion relations connecting the polarization behavior of lower- and higher-order processes. The results are summarized in Sec. III.

To avoid any possible misunderstanding later, we emphasize that, when we discuss the cases involving circularly polarized fundamental waves, we consider the fundamental wave which is normally incident upon the crystal to be circularly polarized and ask the question whether a particular harmonic

TABLE I. Experimental results for nonlinear interaction of circularly polarized radiation. The polarizations are given with respect to the sense of circular polarization of the fundamental in the case of harmonic generation and that of ω_1 in the case of difference-frequency generation, where "opp" corresponds to *opposite* sense of circular polarization and "no" indicates the harmonic is *forbidden*. The absence of an entry signifies no measurement has been reported.

Medium	Symmetry group	Symmetry axis	Harmonics Second	Third	Difference freq. $(\omega_1-\omega_2\rightarrow\omega_3)$
Liquid[a]	3D Rotation	any	$\cdots$	no	$\cdots$
$NaClO_3$[b]	$T(23)$	3	opp	$\cdots$	$\cdots$
$NaBrO_3$[b]	$T(23)$	3	opp	$\cdots$	$\cdots$
Quartz[b]	$D_3(32)$	3	opp	$\cdots$	$\cdots$
Glass[c]	3D Rotation	any	$\cdots$	no	$\cdots$
InSb[d]	$T_d(\bar{4}3m)$	3	$\cdots$	$\cdots$	opp$(\omega_2,\ \omega_3)$

[a]P. P. Bey, J. F. Giuliani, and H. Rabin, Phys. Letters 26A, 128 (1968); R. C. Eckardt and C. H. Lee, Appl. Phys. Letters 15, 425 (1969).

[b]H. J. Simon and N. Bloembergen, Phys. Rev. 171, 1104 (1968).

[c]J. F. Ward and G. H. C. New, Phys. Rev. 185, 57 (1969).

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is forbidden or allowed and if allowed whether it is purely circularly polarized or elliptically polarized, which includes of course the limiting case of linear polarization. Thus, if the harmonic coming out of the crystal is elliptically polarized, we do not determine its ellipticity; that is beyond the scope of the present work. Also, as is well known for noncubic crystals the fundamental wave inside the crystal may not be circularly polarized even for a purely circularly polarized incident wave upon the crystal. This problem in linear optics has been studied in detail in the past (see, for example, Nye[11]). For our purpose, as long as the wave inside the crystal is no longer circularly polarized, it is inconsequential whether it is elliptically polarized or more specially linearly polarized or a linearly polarized rotating wave, etc.; therefore, in what follows we do not specify the specific details of the waves inside the crystal when the waves are not purely circularly polarized.

II. THEORY

A. Harmonic Generation

To illustrate the general procedure, we consider first the case of harmonic generation of an arbitrary order n; the generalization to sum- and difference-frequency generation is straightforward and will be discussed later. The complex amplitude of a component of the induced nonlinear polarization $P_i\,(i=-1,0,1)$ at the nth harmonic is related to the components of the electric field E_i of the fundamental wave through the nonlinear susceptibility in the electric dipole approximation:

$$P_i=\sum_{m_1,m_2\ldots m_n=-1,0,1}\chi_{i,m_1m_2\ldots m_n}E_{m_1}E_{m_2}\ldots E_{m_n}\ . \tag{1}$$

Here we use the tensor notation in which the subscripts -1, 0, and 1 refer, respectively, to the components $(P_x+iP_y)/\sqrt{2}$, P_z, and $-(P_x-iP_y)/\sqrt{2}$ in the case of the nonlinear polarization and similarly for the electric field.

If the z axis is chosen along the direction of propagation of the normally incident fundamental wave which is circularly polarized in one sense only ($m=-1$ or 1), Eq. (1) reduces to

$$P_i=\chi_{i,m\ldots m}(E_m)^n\ . \tag{2}$$

The selection rules or the sense of circular polarization of the nth harmonic is directly determined from P_i, and the sense of circular polarization of P_i, if any, will clearly depend on the nonlinear susceptibility $\chi_{i,m\ldots m}$ for $i=m$ or $-m$: If $\chi_{m,m\ldots m}=0$, the nth harmonic cannot have the same circular polarization as the fundamental; if $\chi_{-m,m\ldots m}=0$, it cannot have the opposite sense of circular polarization; if $\chi_{m,m\ldots m}$ is not required to be zero by symmetry considerations, then the nth harmonic can have the same circular polarization; if $\chi_{-m,m\ldots m}$ is not required to be zero by symmetry, the nth harmonic can have the opposite circular polarization. When both susceptibilities are not required to vanish, the harmonic is elliptically polarized and the sense of rotation will depend upon their relative magnitudes and signs and is not predicted on the basis of symmetry argument alone. These considerations apply equally well to the linear case ($n=1$). In this case, if $\chi_{m,-m}$ is not required to vanish, then the fundamental wave inside the crystal is not circularly polarized even though the fundamental wave incident upon the crystal is circularly polarized. In this case the eigenstate of polarization for wave propagation inside the crystal is elliptical, which includes the special case of linear polarization. This situation always arises in noncubic crystals (i.e., uniaxial or biaxial crystals) along nonprivileged directions.[11] Our problem is, therefore, to determine which $\chi_{i,m\ldots m}$ must be zero for given circular components of the fundamental wave (specified by $m=-1$ or 1) along a given direction in a nonlinear optical crystal of certain symmetry. These results are completely symmetric for either the right- or left-circular component.

The method used to determine which $\chi_{i,m\ldots m}$ must vanish is the following. For a crystal of a given point-group symmetry, we consider all the operations in the group that leave the crystal invariant.

Let the operation be represented by R and the corresponding transformation matrix for tensors of the first rank be $D_{im}^{(1)}(R)$. The explicit form of the $D^{(1)}$ matrix is the following[12]:

$$D^{(1)}(\alpha\beta\gamma)=\begin{pmatrix} \frac{1}{2}(1+\cos\beta)e^{-i(\alpha+\gamma)} & \mp\frac{1}{\sqrt{2}}(\sin\beta)e^{-i\alpha} & \frac{1}{2}(1-\cos\beta)e^{-i(\alpha-\gamma)} \\ \frac{1}{\sqrt{2}}(\sin\beta)e^{-i\gamma} & \pm\cos\beta & -\frac{1}{\sqrt{2}}(\sin\beta)e^{i\gamma} \\ \frac{1}{2}(1-\cos\beta)e^{i(\alpha-\gamma)} & \pm\frac{1}{\sqrt{2}}(\sin\beta)e^{i\alpha} & \frac{1}{2}(1+\cos\beta)e^{i(\alpha+\gamma)} \end{pmatrix}, \quad (3)$$

where α, β, and γ are the three Euler angles corresponding to the operation R, and the lower set of signs refers to improper rotations. Since the components of the nonlinear polarization and the E field in Eq. (1) transform as tensors of the first rank, and the nonlinear susceptibilities in Eq. (1) must be invariant under these operations, it follows that the nonlinear susceptibilities must satisfy the following equation:

$$\sum_{i_1} D_{ii_1}^{(1)}(R)\chi_{i_1,m_1\ldots m_n}=\sum_{j_1,\ldots,j_n}\chi_{i,j_1\ldots j_n} \times D_{j_1m_1}^{(1)}(R)\cdots D_{j_nm_n}^{(1)}(R)\ , \quad (4)$$

for all the R's in the group; those χ's which do not satisfy this equation are not invariant under all the R's and hence must vanish. This equation is analogous to Eq. (II. 3) of Franken and Ward.[13] The essential difference is that here, since we are concerned with circularly polarized light, the complex $D^{(1)}(R)$ matrices appear in place of the real orthogonal R matrices for the Cartesian coordinates.

In the case of harmonic generation, in addition to Eq. (4), $\chi_{i,m_1\ldots m_n}$ must also satisfy the permutation restriction which requires invariance under permutation of the subscripts $m_1, m_2\ldots m_n$. It has been verified that the Kleinman condition[14] for second-harmonic generation does not affect the results reported herein, and this condition for the higher harmonics has not yet been explicitly established; hence, it is not taken into account in the work that follows.

For the present problem, we divide the 32 crystallographic groups[15–17] into three types[16]: cyclic, dihedral, and cubic.

Cyclic-Type Groups

These include the cyclic groups C_1, C_2, C_3, C_4, and C_6, and those groups that are either isomorphic to the cyclic groups or are products of the cyclic groups and the inversion, C_i, C_s, C_{2h}, C_{3i}, C_{3h}, S_4, C_{4h}, and C_{6h}.

We assume that the waves propagate along the axis of highest rotational symmetry; therefore, the z axis also coincides with the axis of highest rotational symmetry of the crystal. For the cyclic-type groups, $x+iy$, z, and $-x+iy$ each forms the basis for an one-dimensional irreducible representation; Eq. (4) then reduces for the cyclic-type groups to

$$D_{ii}^{(1)}(R)\chi_{i,m_1\ldots m_n}=\chi_{i,m_1\ldots m_n}D_{m_1m_1}^{(1)}(R)\cdots D_{m_nm_n}^{(1)}(R)\ , \quad (5)$$

since all the $D^{(1)}$ matrices involved are diagonal in this representation. Physically this corresponds to the requirement that a right- or left-circular polarization remains, respectively, a right- or left-circular polarization under the symmetry operations of these groups. Equation (5) implies that either the condition

$$D_{ii}^{(1)}(R)=D_{m_1m_1}^{(1)}(R)\cdots D_{m_nm_n}^{(1)}(R) \quad (6)$$

is satisfied for all the R's in the group, or if it is not,

$$\chi_{i,m_1\ldots m_n}=0\ . \quad (7)$$

Now since $x+iy$, z, and $-x+iy$ are each the basis of a one-dimensional irreducible representation of the group, the diagonal matrix elements $D_{ii}^{(1)}(R)$ are simply the characters of the corresponding irreducible representation. Whether Eq. (6) is satisfied or not for any particular cyclic-type group can simply be determined from the known characters or the representation multiplication table for that particular group.

For harmonic generation involving purely circularly polarized fundamental waves propagating along the z axis, the problem is reduced in complexity since in such a case $m_1=m_2=\cdots=m_n=m=\pm 1$ and $i=\pm 1$. For any cyclic group of order p,

$$[D_{mm}^{(1)}(R)]^p=1 \quad (8)$$

and

$$D_{-m-m}^{(1)}(R)D_{mm}^{(1)}(R)=1 \quad (9)$$

for all the R's in the group. It immediately follows from these properties, Eqs. (8) and (9), of the cyclic groups that Eq. (6) cannot be satisfied for $m_1 = m_2 = \cdots = m_n = m$, or $\chi_{i,m\ldots m}$ must vanish, unless one or both of the following conditions is satisfied:

$$i = m \quad \text{and} \quad n = pq + 1 \quad (q = 0, 1, 2, \ldots), \tag{10a}$$

$$i = -m \quad \text{and} \quad n = pq - 1 \quad (q = 1, 2, \ldots), \tag{10b}$$

where q is an integer. Thus the selection rules are the following: For a circularly polarized fundamental wave propagating along a p-fold rotational symmetry axis of a nonlinear optical crystal with cyclic point-group symmetry, the allowed $(qp+1)$th harmonic must have the same sense of circular polarization as that of the fundamental wave, and the allowed $(qp-1)$th harmonic must have the opposite sense; all the other harmonics must vanish.

For the special case $p = 1$, since both conditions (10a) and (10b) can always be satisfied simultaneously for all $n(1, 2, 3, \ldots)$, the fundamental wave inside the crystal is no longer circularly polarized and all the harmonics are in general allowed and elliptically polarized. For the case $p = 2$, Eqs. (10a) and (10b) can also be satisfied simultaneously for any odd $n(1, 3, \ldots)$; therefore, the fundamental wave inside the crystal again is no longer circularly polarized, and the odd harmonics are in general allowed and elliptically polarized, while the even harmonics must vanish. Therefore, the situation where a purely circularly polarized fundamental wave propagates inside the crystal along onefold or twofold axes that are not optical axes in the cyclic groups cannot occur; it can only occur in cubic crystals or along optical axes in noncubic crystals. However, it turns out that the selection rules for the harmonics along onefold and twofold axes are independent of the state of polarization of the fundamental wave inside the crystal; the allowed harmonics are always elliptically polarized, which includes the special case of linear polarization.

The remaining cyclic-type groups contain not just rotational symmetry axes, but rotation-reflection or rotation-inversion axes. On the basis of Eqs. (6) and (7), it is clear that the selection rules for the rotation-reflection axes are the same as the corresponding rotational symmetry axes in the context of the present problem. As for the rotation-inversion axes, similar considerations show that, within the context of the present problem, the onefold rotation-inversion axis ($\bar{1}$) behaves like the twofold rotation axis; the twofold rotation-inversion axis ($\bar{2}$) behaves like an onefold rotation axis; the threefold rotation-inversion axis ($\bar{3}$) behaves like the sixfold rotation axis; the fourfold rotation-inversion axis ($\bar{4}$) behaves like a fourfold rotation axis; and the sixfold rotation-inversion axis ($\bar{6}$) behaves like a threefold rotation axis.

Consider next the C_s, S_4, and C_{3h} groups. The C_s group has a twofold rotation-inversion axis; therefore, the fundamental wave inside the crystal is not circularly polarized and all harmonics are allowed and in general are elliptically polarized when the incident fundamental wave is purely circularly polarized around this axis. The S_4 group has a $\bar{4}$ axis; it behaves like a fourfold rotation axis for the present problem. The C_{3h} group contains a $\bar{6}$ axis; it behaves like a threefold rotation axis or $p = 3$ in Eqs. (10a) and (10b).

For the inversion group C_i the matrix elements $D^{(1)}_{mm}$ are either $+1$ or -1; thus, Eq. (6) can be satisfied for all the R's in the inversion group only if n is odd. The even harmonics must, therefore, always vanish; the fundamental wave is no longer circularly polarized inside the crystal and the odd harmonics are in general allowed and elliptically polarized. Thus, for the groups C_{2h}, C_{3i}, C_{4h}, and C_{6h} which are the products of C_i with C_2, C_3, C_4, and C_6, respectively, again the same selection rules that apply to the cyclic groups apply here with the additional requirement that all the even harmonics must vanish. The same results are obtained on the basis of the equivalence of the rotation-inversion or rotation-reflection axes with the appropriate rotation axes as discussed above. The specific results for these groups are given in Table II (see Sec. III).

We consider now explicitly the case when the fundamental wave in the crystal contains both circular polarizations. In that case, on the basis of Eqs. (1) and (6)–(9), it can be shown that for each cyclic group and its corresponding cyclic-type groups the nth harmonic will be allowed and will in general be elliptically polarized if n is equal to $(qp \pm 1)$ plus any integral multiples up to $\frac{1}{2}n$ $(0, 1, 2, \ldots < \frac{1}{2}n)$ of 2; q is any integer $0, 1, 2, \ldots$. Thus, for example, third-harmonic generation is allowed if the fundamental wave is elliptically polarized around a threefold or sixfold rotational symmetry axis but would be forbidden if the fundamental wave is purely circularly polarized. In fact it implies, for example, that all odd harmonics are always allowed whatever the point group if the fundamental wave is elliptically polarized; for some groups, additional even harmonics are of course also allowed depending upon the particular symmetry axis involved.

Dihedral-Type Groups

These include the dihedral groups D_2, D_3, D_4, and D_6; and those groups that are either isomorphic to the dihedral groups, C_{2v}, C_{3v}, D_{2d}, C_{4v}, D_{3h}, and C_{6v}, or are the direct product of the dihedral groups and the inversion, D_{2h}, D_{3d}, D_{4h}, and D_{6h}.

Consider first the dihedral groups and assume that the fundamental wave propagates along the axis

ish. Thus, we conclude that the threefold and twofold axes behave in the same way in the T group as the C_3 and D_2 (or C_2) groups, respectively, as far as the existence and the sense of circular polarization of the nth harmonic of a purely circularly or elliptically polarized fundamental wave are concerned.

Consider next the O group. It has four threefold axes, three fourfold axes, and six twofold axes. There are, therefore, in addition to the operations of T, six operations C_4 and C_4^{-1} and six C_2 operations about the six twofold axes passing through the centers of diagonally opposite cube edges. The operations in the subgroup T have already been considered and found to impose no restrictions on the harmonics in addition to those required by the rotations about the direction of propagation. Consider now the C_4 and C_4^{-1} rotations about the z axis. In the case of second-harmonic generation, these require that the only allowed nonvanishing susceptibilities are χ_{000}, χ_{101}, χ_{-10-1}, χ_{01-1}, χ_{110}, χ_{-1-10}, and χ_{0-11}. In addition, C_4 rotations about the x and y axes require that $\chi_{101} = -\chi_{110}$ and $\chi_{-10-1} = \chi_{-1-10}$, and a C_2 rotation about a twofold axis in the (xy) plane requires that $\chi_{01-1} = -\chi_{0-11}$, which violates the permutation-symmetry condition for harmonic generation; the C_2 rotation also requires $\chi_{000} = -\chi_{000} = 0$. Thus, all the χ's must vanish and second-harmonic generation in crystals with O symmetry is entirely forbidden, which is a well-known fact. We conclude, therefore, that the onefold and threefold axes in the O group behave differently from those of the cyclic- and dihedral-type groups in the case of second-harmonic generation; second-harmonic generation along a twofold, fourfold, or sixfold axis is always forbidden in any case. In the case of higher harmonics, similar considerations will show that the operations in the full group and the permutation symmetry requirement do not impose any additional restrictions on the polarization behavior if the fundamental wave propagates along an arbitrary direction other than one of the symmetry axes; thus, the behavior of the various rotational symmetry axes in the O group is again the same as those in the cyclic- and dihedral-type groups already considered insofar as the polarization of the third or higher harmonics of a purely circularly or elliptically polarized fundamental wave is concerned.

The same conclusions that apply to the T and O groups also apply to the T_h and O_h groups, respectively, with the additional requirement that all the even harmonics must vanish.

Finally, we have the T_d group. It contains four threefold, three twofold, and three fourfold rotation-inversion axes which coincide with the twofold axes. In addition to the operations of the T group, it contains three S_4 and three S_4^{-1} operations and six reflections. The key difference between the T_d group and the O group as far as the present problem is concerned is that in the T_d group we have six S_4 and S_4^{-1} operations rather than the C_4 and C_4^{-1} operations. In the case of second-harmonic generation in the T_d group, the S_4 and S_4^{-1} operations require that the nonvanishing susceptibilities $\chi_{101} = \chi_{110}$ and $\chi_{-10-1} = \chi_{-1-10}$, which do not violate the permutation symmetry condition and hence need not vanish; therefore, the second harmonic does not have to vanish and the twofold and threefold rotation axes and the fourfold rotation-inversion axes in the T_d group behave exactly as the corresponding axes in the cyclic- or dihedral-type groups in the case of second-harmonic generation as well as the higher-harmonic cases.

Three-Dimensional Rotation Group

In addition to the 32 crystallographic groups, the three-dimensional rotation group is also of interest for the case of isotropic media. For this case, Eq. (4) can also be reduced to the form of Eq. (5) and Eqs. (6) and (7) also apply. Here R represents, of course, any infinitesimal or finite rotations of the coordinate axes. It is clear on the basis of the explicit form of the corresponding D matrices that Eq. (6) cannot be satisfied for any $n \geq 2$ if $m_1 = m_2 = \cdots = m_n$. Thus, harmonic generation in isotropic media is always forbidden if the incident wave is purely circularly polarized. On the other hand, if the fundamental wave contains both circular components, it can be shown again on the basis of Eqs. (6) and (9) that all even harmonics are still forbidden but odd harmonics are allowed and in general elliptically polarized. It is clear that these selection rules apply also to the two-dimensional rotation group when the direction of propagation is along the axis of symmetry.

B. Sum- or Difference-Frequency Generation

The main difference for the selection rules in sum-frequency generation and harmonic generation is that, in the former case, the permutation symmetry condition does not have to be satisfied. Thus, on the basis of our previous considerations of harmonic generation, if the n waves to be summed are all purely circularly polarized in the same sense and propagate along a p-fold rotational symmetry axis or its equivalent rotation-reflection or -inversion axis, the sum wave will have opposite sense of circular polarization if $n = qp - 1$ and the same sense of circular polarization if $n = qp + 1$, where q is any positive integer or zero. When both $n = qp + 1$ and $q'p - 1$, where q' is another positive integer, then the sum wave is generally elliptically polarized. For example, in a three-wave collinear-mixing experiment along a fourfold axis of symmetry group C_{4v} the polarization of the summed frequency is opposite in circulation to the common polarization of the three input waves. If the n waves to be summed along a p-fold axis are each elliptically polarized, then any resultant sum waves of the order $qp \pm 1$ plus any integral multi-

if all the component waves are elliptically polarized then the selection rules are the same as those of the sum-frequency case discussed above. If, however, each frequency component is circularly polarized,

have the same polarization as the m waves if $m-n = qp+1$ and the opposite polarization if $m-n=qp-1$; again, if both conditions are satisfied, the sum wave will in general be elliptically polarized.

In the case of difference-frequency generation, where the circular polarizations of the two input waves at ω_1 and ω_2 are opposite. It is only necessary to reverse the sense of polarization of ω_2, and consider then the sum-frequency case of two input waves of the same sense of circular polarization

TABLE II. Selection rules for harmonic generation of arbitrary order using a circularly polarized incident fundamental wave along different axes of symmetry in the 32 crystallographic groups and in isotropic media. For noncubic groups, the selection rules for harmonic waves along onefold or twofold axes that are not optical axes refer to circularly polarized incident fundamental waves which are not circularly polarized inside the medium. The entries are "same" for the harmonic of the *same* sense of circular polarization as the incident fundamental, "opp" for the *opposite* sense, "ellip" for an *elliptically* polarized harmonic (which includes its limiting case of linear polarization), and "no" indicates the harmonic is forbidden with a circularly polarized input. The single asterisk for a given circularly polarized harmonic indicates that the entry corresponds to the same sense of circular polarization as that of the incident fundamental, the next higher-order harmonic then has the same entry as that for the second harmonic (except the O group along a threefold axis), and all successive higher harmonics repeat cyclically thereafter. The O group follows the C_3 group for repetition of entries for the third and higher harmonics along the threefold axis. The double asterisk for a given elliptically polarized harmonic produced by the incident circularly polarized fundamental indicates that the next-higher-order harmonic has the same entry as that for the second harmonic, and the successive higher harmonics are cyclically repeated thereafter in sequence; the sense of elliptical rotation is not implied. *All* harmonics are forbidden for the three-dimensional rotation group (isotropic media) for a circularly polarized fundamental.

Symmetry group	Symmetry axis	Harmonics: Second	Third	Fourth	Fifth	Sixth	Seventh
C_1[a]	1	ellip**	ellip	ellip	ellip	ellip	ellip
C_s, C_{2v}, C_{3v}, C_{4v}, C_{6v}, D_{2d}, D_{3h}, T_d	$\bar{2}(=m)$						
C_2, D_2, D_3, D_4, D_6, C_{2v}, D_{2d}, D_{3h}, T, O	2	no	ellip**	no	ellip	no	ellip
C_i[b]	$\bar{1}$						
C_{2h}, D_{2h}, D_{3d}, D_{4h}, D_{6h}, T_h, O_h	$2/m$						
C_3, D_3, C_{3v}, T, T_d	3	opp					

as that of ω_1. This is the first case cited above for frequency-sum generation. According to Table II the polarization at the summed frequency will be of opposite circulation to that of frequency ω_1. Hence, in the example under consideration the polarization of the difference wave ω_3 is also opposite to that of ω_1, in agreement with observed results.[9]

III. SUMMARY

Table II presents a summary of the selection rules within the electric dipole approximation obtained in Sec. II for harmonic generation employing circularly polarized incident radiation. It should be clearly understood that these results always refer to the situation where the fundamental wave normally incident upon the crystal is circularly polarized; for noncubic groups along onefold and twofold axes which are not optical axes, the fundamental wave inside the crystal is not circularly polarized. Some of the results for second- and third-harmonic generation have been obtained previously[1,2] using different methods. The table gives the characteristics of the second to seventh harmonics and indicates the corresponding behavior of higher harmonics. The tabular arrangement indicates the similarity of behavior of harmonics produced along symmetry axes in the various crystallographic groups to that of the five cyclic groups (C_1, C_2, C_3, C_4, and C_6). For example, for propagation along the fourfold symmetry axis of crystals C_4, D_4, C_{4v}, and O the harmonics produced are identical; that is, a circularly polarized fundamental produces no second or fourth harmonic, the third harmonic is circularly polarized with opposite sense as that of the fundamental, and the fifth harmonic has the same sense of circular polarization as the fundamental. The asterisk indicated for the fifth harmonic shows that all higher harmonics repeat cyclically; the sixth harmonic is forbidden like the second; the seventh is opposite in polarization from the fundamental like the third; the eighth harmonic is forbidden like the fourth, and so on for any higher harmonic.

The table also shows the equivalence of each rotation-inversion or rotation-reflection axis with certain rotation axes within the context of the present problem. For example, exactly the same behavior for the harmonics along a fourfold rotation axis is predicted for propagation along both the $\overline{4}$ axis (i.e., the fourfold rotation-inversion axis) of S_4, D_{2d}, T_d, and O_h and the $4/m$ axis (i.e., the fourfold rotation-reflection axis) of C_{4h} and D_{4h}. In using the table it is necessary to refer always to the *highest* equivalent rotation axis in a given direction in order to determine the properties of the harmonic. In the table it is indicated that $\overline{2}$ is equivalent to a onefold rotation axis, $\overline{1}$ and $2/m$ are equivalent to a twofold axis, $\overline{6}$ (which is identical to $3/m$) is equivalent to a threefold axis (except in the group O), and $6/m$ and $\overline{3}$ are equivalent to a sixfold rotation axis. Thus a direction in a crystal which might have symmetry elements characteristic of both twofold and fourfold axes would be properly described in the table by the fourfold or highest equivalent rotation axis. If a group contains a symmetry axis corresponding to more than one of the equivalent symmetry types in Table II, e.g., $\overline{4}$ or $4/m$, then only a single entry is made since the polarization properties of the harmonic are equivalent for both symmetry types.

As indicated in the table for equivalent onefold and twofold rotation axes a circularly polarized incident fundamental can produce elliptically polarized fundamental and harmonic waves in the crystal. The sense of rotation of the harmonic relative to that of the fundamental is dependent on the relative magnitudes and signs of the appropriate coefficients of the susceptibility tensor, and thus is not specified in Table II. Furthermore, elliptical polarization includes its degenerate or linear form and again this is dependent of the specific susceptibility coefficients and the ellipticity is not specified in the table. It should also be noted that an arbitrary axis in *any* of the noncentrosymmetric crystallographic groups that is not an equivalent twofold rotation axis or higher is a onefold axis; in this case, except for the O group, the tabulated results for the C_1 group should be used. Second-harmonic generation in the O group is strictly forbidden. For an arbitrary (onefold) axis, however, in a centrosymmetric crystallographic group elliptical polarization will result for all odd harmonics and even harmonics are all forbidden in accord with the behavior of the C_i group.

The principal conclusions upon which the table is based can be summarized as follows: For an incident circularly polarized fundamental wave along a p-fold rotation axis, the allowed $(qp-1)$th harmonic always has an opposite circular polarization while the allowed $(qp+1)$th harmonic always has the same circular polarization, where q is an integer. When both of these criteria are satisfied, the harmonic is allowed and elliptically polarized. When neither criteria is satisfied, the harmonic is forbidden. For the harmonics each rotation axis behaves in the same way in all the point groups, except in the O group. For the three-dimensional rotation group all harmonics are forbidden in isotropic media if the input fundamental is purely circularly polarized. In the case of second-harmonic generation, the onefold and threefold axes behave differently in the O group; second-harmonic generation in the O group is forbidden as a result of primarily the permutation symmetry condition. However, for the higher harmonics, all the symmetry axes in the O group again behave in the same way as those of the other point groups. In the same context, the rotation-inversion or rotation-reflection axis always behaves in the same way in all the point groups. Each rotation-inversion or rotation-reflection axis has an equivalent rotation axis as was pointed out above; in fact, this equivalence applies to sum- and difference-frequency generation as well as harmonic generation.

In the case when either the incident fundamental wave is elliptically polarized or the fundamental wave inside the crystal is elliptically polarized, even if the fundamental wave incident upon the crystal is circularly polarized and propagates along a p-fold axis of any of the groups considered, any harmonics of the order equal to $(qp \pm 1)$ plus any integral multiplies (0, 1, 2,...) of 2 are allowed. It implies, for example, that all odd harmonics are allowed in all crystal classes or in media characterized by the three-dimensional rotational group if the incident fundamental wave is elliptically polarized. On the other hand, even harmonics are allowed only along odd rotational symmetry axes but forbidden along all even rotational symmetry axes if the incident wave is elliptically polarized; again, the onefold and threefold axes of the O group are the exceptions in the sense that second-harmonic generation is not allowed whatever the state of polarization of the input along this axis.

Table II may also be employed to determine if sum- or difference-frequency generation is allowed, and the polarization of the radiation produced is determined from the symmetry of the medium along a particular symmetry axis. These results can be of interest in such applications as parametric amplification or oscillation and upconversion. The method of determining polarization properties of circularly and elliptically polarized waves in the sum- and difference-frequency mixing case has been summarized in Sec. II B and is not repeated here.

It should be understood that the selection rules obtained here refer to the case where the electric dipole approximation is valid and where the interacting waves are collinear and the state of polarization of these waves is specified with respect to a collinear axis within the medium which is assumed to be homogeneous and transparent. The results are applicable to other situations not explicitly considered here. For example, in cases where external perturbations such as electric, magnetic, or mechanical methods are employed to alter the symmetry of the nonlinear medium, the results can be used to determine the effect of the change of symmetry. The results may also find analogous applications in cases involving other nonlinear processes, which are not purely of an electromagnetic character.

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