HARMONIC GENERATION AND SELECTION RULES IN NONLINEAR OPTICS

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ABSTRACT

A simple procedure, based on the transformation properties of the nonlinear susceptibility tensors of different ranks referred to appropriate coordinate systems, is given for studying the selection rules and polarization characters in regard to all orders of harmonics. By this procedure, results covering both linearly and circularly polarized incident light for all the 32 crystal classes with some simplifying restrictions are obtained and listed in the paper. Attention is drawn to special features in each case. There is complete agreement with what has been reported earlier by Tang and Herbert Rabin for circularly polarized incident light.

1. INTRODUCTION

FROM an experimental point of view, it is of interest to consider using (i) linearly polarized incident light and (ii) circularly polarized incident light for the generation of harmonics in nonlinear optics relating to crystalline media of different symmetry properties. The phenomena due to circularly polarized incident light are different from those due to linearly polarized light and, because of the nonlinearity, the former cannot be obtained from the latter or *vice versa*, by a simple process of superposition. The two cases are therefore to be studied independently. Tang and Rabin (1971) have considered the problem of circularly polarized incident light and obtained many interesting results. In this paper, we have developed a simple procedure, based on the transformation properties of the nonlinear susceptibility tensors of different ranks referred to appropriate coordinate systems. By this procedure, we have obtained the results in a comprehensive manner, covering both linearly and circularly polarized incident light for all the 32 crystal classes. As it should be expected, there is complete agreement with what has been reported by earlier authors, particularly by Tang and Rabin, for circularly polarized incident light. Complex cases, where the transmission is not along a chosen symmetry axis or where the state of polarization of the generated harmonic bears no simple relation to that of the incident light, are not dealt with in this paper as there is not much interest attached to them in practice.

2. THEORY

The polarization P of a nonlinear dielectric due to an applied electric field E may be written as in (1).

$$P_i = \alpha_i^{j} E_j + \alpha_i^{jk} E_j E_k + \alpha_i^{jkl} E_j E_k E_l + \cdots \qquad (1)$$

P_i, etc., and E_j, etc., are the components of P and E in a general coordinate system. α_i^j of the first term is the linear susceptibility tensor and the α's in the second term onwards represent the nonlinear susceptibility tensors of higher ranks. Summation over the repeated indices is implied. We have taken the polarization and electric field to be covariant vectors so that the susceptibility tensors are of the mixed type. For example, α_i^{jk} is covariant in one index and contravariant in the other two. Such a distinction between covariant and contravariant indices disappears when we consider the special case of a cartesian coordinate system.

The form of the susceptibility tensors depends on the coordinate system chosen. This choice should be made to suit the particular physical problem under consideration. In the case of linearly polarized incident light, a cartesian coordinate system, x, y, z numbered 1, 2, 3 respectively is the most convenient choice. We choose the axis in such a way that the incident light propagates along the z-axis and is polarized along either the x- or the y-axis. When linearly polarized light as specified above is incident upon the crystal and the propagation is taken to be along the principal symmetry axis (along one of the cubic axes in the case of the cubic classes), we seek to know the selection rules and polarization characters for harmonic generation in the 32 crystal classes. It is presumed that observation is always made in the forward direction, *i.e.*, along the direction of propagation.

Neumann's principle requires that every physical property of a crystal should exhibit at least the symmetry of that crystal. Consequently, a tensor representing harmonic generation of a particular order in a nonlinear crystal with a certain point group symmetry must be invariant under all the symmetry operations of that point group. The presence or absence of a particular harmonic in our problem and its state of polarization are thus dictated by whether the appropriate tensor components have a non-zero value or not. As an illustration, we may cite the well-known result that in a centrosymmetric crystal, all components of the tensor α_i^{jk} are zero and hence the second harmonic is not present in these crystals.

The procedure for determining the number of non-zero components of a tensor and the components themselves, subject to a point group symmetry, is a straightforward one and has been given elsewhere (Bhagavantam, 1966). In a general coordinate system x_1, x_2, x_3 under a transformation given by equations like (2),

$$x_i' = A_i^j x_j \tag{2}$$

the tensor components transform as in (3).

$$a_i^{jk} = A_i^p A_q^j A_r^k a_p^{qr}. \tag{3}$$

In the special case of cartesian coordinates, we do not distinguish between the contravariant and covariant indices and write the transformation of the tensor components as in (4).

$$a'_{ijk} = A_{pi}A_{qj}A_{rk}\, a_{pqr}. \tag{4}$$

It is thus possible, with the help of the above transformation laws and Neumann's principle, to write out *in extenso* the non-zero components of the corresponding tensor and study the features of harmonic generation of any order. For instance, in the example of third harmonic generation (THG), a tensor a_{ijkl} of rank 4 and intrinsic permutation symmetry in all the three indices *jkl*, represents the relevant physical property. The corresponding character of transformation is given in (5) and by the methods described earlier (Bhagavantam, 1972) one can find the number of non-zero components

$$\chi(R_\phi) = 8\cos^4\phi \pm 12\cos^3\phi + 8\cos^2\phi \pm 2\cos\phi \tag{5}$$

for each of the crystal classes. The maximum number in this case that is appropriate for the triclinic asymmetric class is 30. Maker, Terhune and Savage (1964) have listed explicitly all the non-zero components of such a tensor for each of the 32 crystal classes and their table can be readily used for arriving at the results regarding THG.

However, in our particular problem the restrictions regarding which have already been stated, we are not interested in all the non-zero components of the susceptibility tensor. Taking the simplest example of second harmonic generation (SHG), the components we need to study are only a_{111}, a_{211}, a_{122} and a_{222}. If, for example in a particular crystal, $a_{111} \neq 0$ and remains invariant for all the generating operations of the point group appropriate to the crystal, it means that incident light polarized in the x direction gives rise to a second harmonic with the same polarization. If $\alpha_{211} \neq 0$ in a similar manner, we get a second harmonic polarized along y. Since the observation is confined, to the z direction , harmonics present due to non-zero values of components like α_{311} and α_{322} are not observed. We may find instances when $\alpha_{111} \neq 0$ and transforms into a linear combination with other components like α_{211} under the application of one of the generating operations. In such a case, the harmonic is expected to be present and exhibit elliptic polarization. We can extend these considerations to harmonics of any order and note that we need to study the behaviour of components like $\alpha_{i11} \ldots$ and $\alpha_{i22} \ldots$ where i can take the values 1 and 2 only.

3. Results with Incident Linearly Polarized Light

The results obtained for the 32 crystal classes are given in Table I. In this, 0 under a particular harmonic signifies that the harmonic is forbidden in all crystals having point group symmetries against which 0 is shown.

TABLE I

Linearly polarized light

Cyclic group C_p	Other groups akin to C_p			Order of harmonic 2	3	4	5	6	7
C_1		C_s		×					
C_2	C_i	C_{2h}		0	×				
	C_{2v}	D_2	D_{2h}	0	+				
	T	T_h							
C_3	C_{3h}			×	×	×			
	C_{3v}	D_3	D_{3h}	+	+	+			
C_4	C_{4h}	S_4		0	×	0	×		
	C_{4v}	D_4	D_{4h}	0	+	0	+		
	D_{2d}								
	T_d	O	O_h						
C_6	C_{6h}	C_{3i}		0	×	0	×	0	×
	D_{3d}	C_{6v}		0	+	0	+	0	+
	D_6	D_{6h}							
	3D			0	+	0	+	0	+

A + sign indicates that the harmonic is present and that its state of polarization is preserved, *i.e.*, it is linearly polarized along the axis which is the same as the one along which the incident light is polarized. An × sign means that in addition to a component along the direction of polarization of the incident light, there is also a component of that particular harmonic polarized in a direction perpendicular to it giving in general, elliptically polarized light. Results for the 3-dimensional rotation group (Isotropic medium) are also included. For the cyclic group C_p and other groups akin thereto, results are given only up to the harmonic of order $p+1$ because in each case, the pattern is found to repeat itself thereafter.

We observe the following points of interest. Even harmonics are absent in the cyclic groups C_2, C_4, C_6, in the related groups and in the 3-dimensional rotation group. There is no group in which a linearly polarized harmonic is present with its direction of polarization different from that of the incident light. Addition of a mirror plane σ_h perpendicular to the z-axis does not change the selection rules. On the contrary, the additions of a dihedral axis or a σ_v plane parallel to the z-axis reduces elliptically polarized light to linearly polarized light. In all such cases, we have chosen the coordinate axes such that the incident light is polarized either along the dihedral axis or along an axis parallel to the plane.

4. Results with Incident Circularly Polarized Light

Once again we shall take the propagation to be along the principal symmetry axis, and the incident light is either right circularly polarized or left circularly polarized with respect to the direction of propagation, along which the observation is being made. The coordinates chosen are defined by

$$x+iy, \quad x-iy, \quad z$$

and numbered successively as 1, 2, 3.

In this system, the components of the incident light vector are:

$$E_1 = E_x + iE_y\ ;\ E_2 = E_x - iE_y.$$

E_1 and E_2 may be regarded as respectively representing left and right circularly polarized light. Under a rotation through an angle ϕ about the z-axis, the coordinates transform as:

$$E_1' = e^{-i\phi}E_1;\ E_2' = e^{i\phi}E_2;\ E_3' = E_3.$$

We observe that the transformation matrix for this set of coordinates is diagonal. The tensor components transform under such a rotation as in (3). In this case, it is necessary to distinguish between contravariant and covariant indices. Taking the second harmonic as an illustration, once again we are interested only in components like α_1^{11}, α_2^{11}, α_1^{22} and α_2^{22}. In the case of higher harmonics also, we need consider only components of this kind. The transformation laws for these components are (for a p-th harmonic given by the component $\alpha_{1\text{ or }2}^{111\cdots}$ p-times)

$$\alpha'^{11\cdots}_1 = e^{i\phi}\, e^{-ip\phi}\, \alpha_1^{11\cdots} = e^{-i(p-1)\phi}\, \alpha_1^{11\cdots}$$

$$\alpha'^{11\cdots}_2 = e^{-i\phi}\, e^{-ip\phi}\, \alpha_2^{11\cdots} = e^{-i(p+1)\phi}\, \alpha_2^{11\cdots}.$$

If $\alpha_1^{11\cdots}$ survives in a particular point group, it means that the corresponding p-th harmonic is present, and that left circularly polarized light gives a left circularly polarized harmonic. If $\alpha_2^{11\cdots}$ is present, it means that left circularly polarized light gives a right circularly polarized harmonic. Analogous results hold good for right circularly polarized incident light. In fact, the problem is completely symmetric with regard to right and left circular polarization.

The results for circularly polarized incident light are summarized in Table II. A 0 under a particular harmonic indicates that the harmonic is forbidden in crystals of that particular symmetry. A + sign signifies that the harmonic is present and the polarization is the same as that of the incident light. A – sign signifies that a right circularly polarized incident light gives a left circularly polarized harmonic and *vice versa*. A × sign indicates the presence of both states of polarization giving in general, elliptically polarized light.

For the cyclic groups, we arrive at the following rules from the transformation laws for the tensor components:

If

$$p - 1 = 2n\pi/\phi,$$

we obtain a + sign indicating that the polarization is preserved.

If

$$p + 1 = 2n\pi/\phi,$$

we obtain a – sign indicating that the polarization is reversed.

If neither of the above conditions is satisfied, we obtain a 0 sign indicating that the harmonic is forbidden. n in the foregoing relations is any integer and the symmetry operation for the group is a rotation through the angle ϕ about the z-axis.

TABLE II

Circularly polarized light

Cyclic group C_p	Other groups akin to C_p			Order of Harmonic 2	3	4	5	6	7
C_1		C_s		×					
C_2	C_i	C_{2h}	C_{2v}	0	×				
	D_2	D_{2h}							
	T	T_h							
C_3	C_{3v}	C_{3h}		–	0	+			
	D_3	D_{3h}							
C_4	C_{4h}	C_{4v}		0	–	0	+		
	S_4	D_4	D_{4h}						
	D_{2d}								
	T_d	O	O_h						
C_6	C_{6h}	C_{6v}		0	0	0	–	0	+
	D_6	D_{6h}							
	C_{3i}	D_{3d}							
	3D			0	0	0	0	0	0

It may be seen that even harmonics are absent in the centro-symmetric groups and in C_2, C_4, C_6 and the 3-dimensional rotation group. Addition of a dihedral axis or a mirror plane σ_h does not change the selection rules. None of the harmonics are present in the 3-dimensional rotation group. It is interesting to note that unlike in the case of incident linearly polarized light, the selection rules in this case are not the same for all the five cubic classes. For instance, third harmonic in the classes T and T_h is elliptically polarized whereas it is circularly polarized (opposite to the sense of the incident light) in the classes T_d, O and O_h. That this distinction does not exist in the linearly polarized case may be seen from Table I. That the five classes in the cubic system of crystals fall into two such groups for some chosen physical properties was first recognised and pointed out by one of us in connection with a study of crystal symmetry in relation to photo-elasticity (Bhagavantam, 1942).

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