CRYSTAL SYMMETRY AND NONLINEAR OPTICAL PROPERTIES

By S. Bhagavantam, F.A.Sc.

(*Indian Institute of Science, Bangalore–12, India*)

Received October 14, 1971

ABSTRACT

In an introductory section, the symmetry properties of some of the higher rank polar tensors relating to nonlinear optical polarization are briefly enumerated. It is noted that linear magneto-electric polarizability has been experimentally measured and that the reported results are in conformity with the theory. Symmetry properties of the higher rank axial tensors relating to nonlinear magneto-electric effect are enumerated and it is suggested that such an effect is possible in some crystals in the anti-ferromagnetic state. In all these studies, methods developed earlier by the author have been used.

1. Introduction

A PHYSICAL property, almost always expresses the relation between two measurable physical quantities. Each such physical quantity can be regarded as a tensor of an appropriate kind and rank. In equation (1), $A_{lmn\ldots}$ and $B_{ijk\ldots}$ are tensors representing physical quantities and $a_{ijk\ldots lmn\ldots}$ is the tensor representing the physical property connecting them. If $A_{lmn\ldots}$, the influence tensor is of rank p and $B_{ijk\ldots}$, the effect tensor is of rank q, the physical property $a_{ijk\ldots lmn\ldots}$ must be a tensor of rank $(p+q)$.

$$B_{ijk\ldots} = a_{ijk\ldots lmn\ldots} A_{lmn\ldots} \qquad (1)$$

Thus we can associate with every physical property, a tensor of an appropriate kind and rank. In a crystal belonging to a particular class, all physical properties represented by a tensor of the same kind and rank possess the same scheme of non-vanishing coefficients. The usefulness and convenience of such a broad classification and general treatment, particularly in studying the effect of crystal symmetry on physical properties, have been fully explained and exploited in a recent book written by the author (1966).*

* This book is cited as reference 1 in the rest of the paper.

Tables containing details about many known physical properties in regard to all the crystal classes have been given in that publication. Some tensors, in respect of which representative physical properties are not readily available, have also been listed in the tables.

2. Nonlinear Effects: Polar Tensors

Relation (1) is linear in the tensor components and can be regarded only as a first approximation. When nonlinear effects begin to appear, we have to introduce quadratic and higher power terms and tensors of higher ranks as multiplying factors on the right hand side of (1). This has already been done very extensively in the case of a few well studied physical properties such as third order elasticity and the like. However, with the advent of high intensity light beams obtained by laser action, nonlinear optics and harmonic generation have come to be studied vigorously in recent years. To take account of such phenomena, the polarization P or the electric moment induced per unit volume should be expressed as in (2).

$$P_i = a_{ij}E_j + a_{ijk}E_jE_k + a_{ijkl}E_jE_kE_l \ldots \qquad (2)$$

The first term defines the linear polarizability, the second term defines the lowest order nonlinear polarizability and so on. P and E are vectors while a in the first, second and third terms will in general be a tensor of second, third and fourth rank respectively. The intrinsic symmetry, if any, in each case has to be determined only after knowing the parameters in respect of the E vectors. All indices take the values 1, 2 and 3 and may be associated with x, y and z axes either in space or of a crystal. The convention of summation over the repeated index is implied. In the general case, a component of E say E_x, representing a linearly polarized light wave, may be written as in (3).

$$E_x = E \exp.(ikz - iwt) + E^* \exp.(-ikz + iwt). \qquad (3)$$

In (2), the two physical quantities P and E are two polar vectors. The physical property that relates them linearly is a second rank polar tensor a_{ij} with the intrinsic symmetry $ij = ji$, provided we are dealing with non-magnetic structures.

a_{ijk} is on a different footing. This is in general a polar tensor of third rank with no intrinsic symmetry and represents the physical property of sum frequency generation in nonlinear polarization of the lowest order. For this to be valid, the incident field should consist of two light waves of two different frequencies w_1 and w_2. Bloembergen (1969) drew attention to the fact that this property of sum frequency generation in nonlinear polarization is a physical example to fill an empty slot in line 6 of Table VII (*a*) in reference 1. a_{ijk} need not be symmetric in any pair of indices and in such a general case, has 27 independent coefficients if the cystal has no symmetry of any kind. We should, however, note that this tensor connects three polar vectors P, E (w_1) and E (w_2).

Nonlinear optics furnishes several other interesting examples and Bloembergen, amongst others, has discussed the special case of second harmonic generation ($w_1 = w_2$) resulting in $a_{ijk} = a_{ikj}$. The tensor in such a case has symmetry properties identical with those of the piezoelectric tensor. Bloembergen (1969) has also pointed out that two particular cases of the fourth rank nonlinear polarization tensor a_{ijkl}-incident field consisting of three light waves at all different frequencies w_1, w_2 and w_3 resulting in 81 maximum number of coefficients in the tensor and the same with the limitation $w_2 = w_3$ resulting in 54 maximum number of coefficients in the tensor —again furnish physical examples of the kinds of tensors listed in lines 10 and 9 respectively of Table VII (*a*) in reference 1. The case of third harmonic generation ($w_1 = w_2 = w_3$) on the other hand, would constitute a physical property represented by a third rank polar tensor, not enumerated in that table. It will be symmetric in all the three indices *jkl* and will consist of a maximum number of 30 non-vanishing coefficients. Maker, Terhune and Savage (1964) have listed explicitly such coefficients in the tensor for each of the 32 crystal classes. The symmetry properties of all these higher rank tensors representing various physical properties dealing with different kinds of nonlinear optical effects, can be dealt with and studied with reference to different crystal classes, by the same methods as have been used by the author for other similar types. For instance, the result that sum frequency generation is possible in a crystal of the cubic class 0 or 432, even though it is not piezoelectric and does not allow second harmonic generation, is contained in Table VIII (*a*) of reference 1. From this table, the number of non-vanishing coefficients for this crystal class is seen as 1 under the column relating to property No. 6 (general case of product of three polar vectors). We should therefore conclude that sum frequency generation is possible. On the other hand, the number is 0 under the column relating to property No. 5 (special case of piezoelectricity). We should therefore conclude that second harmonic generation is not possible.

3. Nonlinear Effects: Axial Tensors

So far, we have commented on various nonlinear polarization properties, represented by polar vectors and polar tensors of higher ranks. These have been hitherto intensively studied. The purpose of the present paper is to examine some other physical properties in the realm of nonlinearity, which had not received such attention in the past and which are represented by axial vectors and axial tensors. There is a special interest in examining such cases as it leads us to look for such effects in crystals of the magnetic class (Shubinkov groups). We may write equation (4), where the magnetic moment I takes the place of P of equation (2).

$$I_i = \lambda_{ij}E_j + \lambda_{ijk}E_jE_k + \lambda_{ijkl}E_jE_kE_l \ldots \tag{4}$$

This equation describes the production of magnetic moment I in a crystal by the application of electric fields E. Taking the first term, we note that λ_{ij} is the tensor representing a physical property called the magneto-electric polarizability, observable in certain crystals in their antiferromagnetic state. The tensor connects two physical quantities E and I which are respectively a polar and an axial vector. The symmetry properties of λ_{ij} have been examined in detail in the book already cited as reference 1 and explicit forms in the 58 magnetic classes in which it is non-zero have been given. This effect has been observed and measured in chromium oxide in its anti-ferromagnetic state, the crystal class being $\bar{3}\underline{m}$. It has been found that there are two independent non-zero coefficients in λ_{ij} and this is in accordance with what may be expected from the theory (Dzyaloshinski, I. E., 1960; Astrov, D. N., 1961).

λ_{ijk} on the other hand is analogous to a_{ijk} and represents the physical property of the lowest order nonlinear magnetic polarization caused by the application of electric fields. Unlike a_{ijk} which is a product of three polar vectors, λ_{ijk} is the product of one axial vector and two polar vectors. Accordingly, the latter is a third rank axial tensor. Further, it represents a magnetic property. This difference between a_{ijk} and λ_{ijk} in two important respects results in their symmetry properties being very different. In the case of a_{ijk}, consideration of the magnetic classes becomes redundant as no new results can be expected whereas λ_{ijk} can have non-zero coefficients only if the crystal has a symmetry appropriate to a magnetic class. Main features are summarised in Table I. All four cases relate to nonlinear polarization caused by two light beams ($w_1 \neq w_2$ in the first two and $w_1 = w_2$ in the last two) acting on the crystal.

The manner of evaluating the character χ(R) in respect of a symmetry operation R and the use of the alternative *plus* and *minus* signs appearing therein are fully explained in reference 1. The number under $n_i^{\max.}$ is the

TABLE I

Tensor	Property	Character χ (R)	$n_i^{max.}$	Possible in
α_{ijk}	Sum frequency generation	$(\pm 1 + 2c)^3$	27	All piezoelectric classes and in 432
λ_{ijk}	Magnetic polarization	$\pm (1 \pm 2c) \times (\pm 1 + 2c)^2$	27	All piezomagnetic classes and some more
α_{ijk} $(jk = kj)$	Second harmonic generation	$(\pm 1 + 2c) \times (4c^2 \pm 2c)$	18	All piezoelectric classes only
λ_{ijk} $(jk = kj)$	Magnetic polarization	$\pm (1 \pm 2c) \times (4c^2 \pm 2c)$	18	All piezomagnetic classes only

maximum number of non-vanishing coefficients in respect of each tensor when we are considering a crystal with no symmetry of any kind. If the crystal has some symmetry, this number gets reduced. The number of non-vanishing independent coefficients in a chosen tensor for a given crystal class is obtained from the relation (5).

$$n_i = \frac{1}{N} \sum_{\rho} h_\rho \chi_\rho (R) \tag{5}$$

N is the order of the crystal point group and the summation extends over all the elements in the group. The two tensors λ_{ijk} and λ_{ijk} $(jk = kj)$ contained in Table I being magnetic in nature, cannot have any non-vanishing coefficients in the para or diamagnetic crystals. We need therefore consider only the 90 magnetic classes, while studying properties represented by these tensors. Results have been obtained in all the 90 classes, but those in respect of the eleven magnetic variants in the cubic class only are given in Table II. Numbers under γ_{ij} refer to the first order or linear magneto-electric polarization. They are taken from the author's book (reference 1) and included here for completeness.

4. Nonlinear Magneto-electric Polarizability

We may note that there are several classes of crystals (m3 and $\underline{432}$ are two examples) in which while the linear magneto-electric effect is not possible we may expect to find the same due to nonlinear polarization, when two light beams are incident with or without the special condition $w_1 = w_2$. While

TABLE II

Physical property / Crystal class	λ_{ij}	$\lambda_{ijk}\ (jk = kj)$	λ_{ijk}
23	1	1	2
m3	0	1	2
$\underline{\mathrm{m}}3$	1	0	0
$\bar{4}3\mathrm{m}$	0	0	1
$\underline{\bar{4}}3\underline{\mathrm{m}}$	1	1	1
432	1	0	1
$\underline{4}3\underline{2}$	0	1	1
m3m	0	0	1
$\underline{\mathrm{m}}3\underline{\mathrm{m}}$	1	0	0
$\mathrm{m}3\underline{\mathrm{m}}$	0	1	1
$\underline{\mathrm{m}}3\mathrm{m}$	0	0	0

this is a formal result concerning the symmetry aspects only, we should note that in practice, in order that the generation of a magnetic moment may be effective, there should be a D.C. component in the nonlinear polarization. The most favourable conditions for such a situation are seen from relation (3) to be $E_1 = E_2^*$ and $w_1 = -w_2$. The production of such a D.C. component in nonlinear optics has been observed and the details studied by several authors (Franken, P. A., 1964).

Two of the cubic magnetic classes, namely, $\bar{4}3\mathrm{m}$ and m3m may be specially mentioned, as in these cases, we may expect to observe the appearance of a magnetic moment as a result of nonlinear sum frequency generation of a general type, while the linear effect as well as the symmetric type effect are forbidden by crystal symmetry.

References

1. Astrov, D. N. .. *Soviet Physics JETP*, 1961, **13**, 729.
2. Bhagavantam, S. .. *Crystal Symmetry and Physical Properties*, Academic Press, 1966.
3. Bloembergen, N. .. "Symmetry properties of nonlinear optical susceptibilities," *Physics of the Solid State*, Academic Press, 1969,
4. Dzyaloshinski, I. E. .. *Soviet Physics JETP*, 1960, **10**, 628.
5. Franken, P. A. .. *Proc. Third Int. Conf. on Quantum Electronics*, Dunod, Paris, 1964, p. 1495.
6. Maker, P. D., Terhune, R. W. and Savage, C. M. *Ibid.*, Paris, 1964, p. 1559.