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Invariants of the Third-Rank Cartesian Tensor: Optical Nonlinear Susceptibilities

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Optical nonlinearities in crystals are for the first time analyzed from the rotational-invariance point of view. Several previous theoretical results are discussed on the basis of the decomposition of a tensor into irreducible parts. A proportionality between the spontaneous polarization and the vector parts of the nonlinearities is established, leading to new relations for the second-harmonic generation and linear electrooptic-effect coefficients in the δ formulation.

I. INTRODUCTION

The optical properties of crystals can be described by the constitutive relations between electromagnetic field and induced polarizations. The linear properties are, for instance, determined by the second-rank tensor $\overleftrightarrow{\chi}$ relating the electric field $\vec{E}$ and the polarization $\vec{\mathcal{P}}$

$$\vec{\mathcal{P}}(\omega) = \overleftrightarrow{\chi} \cdot \vec{E}(\omega) \ . \tag{1}$$

The tensor $\overleftrightarrow{\chi}$ characterizes intrinsic properties of a given material which, unlike the components χ_{ij}, is not affected by a change of the coordinate system. In nondissipative and nonoptically active media there are in general six independent χ_{ij}. Nevertheless, all the linear optical properties can be described in terms of the three principal susceptibilities, directly deduced from the three scalar invariants of $\overset{\leftrightarrow}{\chi}$.[1,2] Three other quantities give the relative orientation of the index ellipsoid with respect to the coordinate system.

The lowest-order optical nonlinearities such as frequency-mixing phenomena or parametric processes arise from the polarization $\vec{\mathcal{P}}(\omega_3)$ related to the electric fields $\vec{E}(\omega_1)$ and $\vec{E}(\omega_2)$ by

$$\vec{\mathcal{P}}(\omega_3=\omega_1+\omega_2)=2\underline{d}(\omega_3,\ \omega_1,\ \omega_2):\vec{E}(\omega_1)\vec{E}(\omega_2), \quad (2)$$

where $\underline{d}$ is a third-rank tensor, and where $\vec{E}(\omega_1)\vec{E}(\omega_2)$ is the direct product of $\vec{E}(\omega_1)$ and $\vec{E}(\omega_2)$.

We present in this paper the decomposition of a third-rank tensor in irreducible tensors based on the three-dimensional rotation group which leads to the definition of scalar invariants of $\underline{d}$. We then apply the results to find specific relations among the second-harmonic generation (SHG) coefficients $d_{ijk}(2\omega, \omega, \omega)$ and among the linear electrooptic effect (LEO) coefficients $d_{kji}(0, \omega, \omega)$.[3]

The decomposition can be applied as well to other physical processes like piezoelectricity or extended to higher-order phenomena. Irreducible spherical tensors have been also successfully introduced for interpreting second-harmonic light scattering in liquids.[4]

II. IRREDUCIBLE PARTS OF THIRD-RANK TENSOR

The decomposition of a Cartesian rank-n tensor as the sum of parts of weight J ($J=0, 1, 2, \ldots, n$) irreducible under the three-dimensional rotation group has been considered by several authors.[5,6] It has been shown that an irreducible representation of rank n and weight J has $2J+1$ independent components and can be expressed in terms of an irreducible tensor of rank J. According to Schouten's notation,[5] the irreducible tensors of rank 0, 1, 2, 3 corresponding to $\underline{d}$ are, respectively, called pseudoscalar, vector, pseudodeviator, and septor. A pseudodeviator is a symmetric and traceless second-rank tensor; a septor is a fully symmetric and traceless third-rank tensor. The traces or the contractions of a third-rank tensor are the vectors

$$\textstyle\sum_j d_{ijj},\ \sum_k d_{kjk},\ \sum_i d_{iik}.$$

In a general way, it is possible to consider $\underline{d}$ as the sum

$$\underline{d}=\underline{d}^{(0)}+\underline{d}^{(1)}+\underline{d}^{(2)}+\underline{d}^{(3)}=\textstyle\sum_J \underline{d}^{(J)}\ , \quad (3)$$

where $\underline{d}^{(J)}=\underline{d}^{(J,1)}+\cdots+\underline{d}^{(J,m_J)}\ ,\quad (4)$

m_J being the number of independent weight J tensors involved in the decomposition.

For a crystal of lowest symmetry (point group 1) there are no symmetry requirements on the d_{ijk} when the three frequencies ω_1, ω_2, and ω_3 are different (asymmetric case); but for SHG and LEO two frequencies are the same and the coefficients of $\underline{d}$ are symmetric in the two last indices (symmetric case). Further simplification occurs when the crystal is nondispersive; as shown by Kleinman[7] d_{ijk} does not depend on the permutations of the three indices i, j, k (fully symmetric case). The numbers m_J corresponding to the three different cases are indicated in Table I.

We now express the tensors $\underline{d}^{(J)}$ in terms of the components d_{ijk} using the technique of Coope *et al.*[6]

A. Pseudoscalar

To the irreducible tensor of weight 0 corresponds a pseudoscalar A according to[6]

$$\underline{d}^{(0)}=\tfrac{1}{6}A\underline{e} \quad (5)$$

where $\underline{e}$ is the completely antisymmetric third-rank tensor[8] and A the quantity defined by

$$A=d_{123}+d_{231}+d_{312}-d_{132}-d_{213}-d_{321}$$
$$=-\sum_{i,j,k} e_{ijk}d_{kji}\ . \quad (6)$$

The term A is responsible for frequency mixing in liquids[9] and obviously vanishes for the symmetric and fully symmetric cases.

B. Vectors

It is well known[1] that any contraction (or trace) of a tensor is irreducible under the rotation group. For $\underline{d}$ there are three contractions, which are the following vectors:

$$V_i^1=\textstyle\sum_j d_{ijj}\ , \quad (7)$$

$$V_j^2=\textstyle\sum_k d_{kjk}\ , \quad (8)$$

$$V_k^3=\textstyle\sum_i d_{iik}\ . \quad (9)$$

The contractions are the only independent vectors. The three weight-1 third-rank tensors of the

TABLE I. Decomposition of a third-rank tensor in irreducible parts according to the symmetries in the indices. The number N of independent coefficients d_{ijk} can be deduced from $N=\Sigma_J(2J+1)m_J$.

Case	m_0	m_1	m_2	m_3	N
Asymmetric	1	3	2	1	27
Symmetric	0	2	1	1	18
Fully symmetric	0	1	0	1	10

decomposition (4) are, using the second-rank unit tensor u_{ij},[10] given by

$$d^{(1,1)}_{ijk}=\tfrac{1}{10}\,(4V^1_i u_{jk}-u_{ik}V^1_j-u_{ij}V^1_k)\,, \tag{10}$$

$$d^{(1,2)}_{ijk}=\tfrac{1}{10}\,(-V^2_i u_{jk}+4u_{ik}V^2_j-u_{ij}V^2_k)\,, \tag{11}$$

$$d^{(1,3)}_{ijk}=\tfrac{1}{10}\,(-V^3_i u_{jk}-u_{ik}V^3_j+4u_{ij}V^3_k)\ . \tag{12}$$

In the symmetric case it is easy to see from Eqs. (8) and (9) that $\vec{V}^2=\vec{V}^3$; when Kleinman's relations hold (fully symmetric case) there is only one vector $\vec{V}$ ($\vec{V}=\vec{V}^1=\vec{V}^2=\vec{V}^3$) and

$$d^{(1)}_{ijk}=\tfrac{1}{5}\,(V_i u_{jk}+u_{ik}V_j+u_{ij}V_k)\ . \tag{13}$$

C. Pseudodeviators

Two pseudodeviators $\overleftrightarrow{D}^1$ and $\overleftrightarrow{D}^2$ (each of them having five independent components) are involved in the decomposition of a third-rank tensor in irreducible parts; they are

$$D^1_{ij}=-\tfrac{1}{2}\sum_{l,m}\,(e_{ilm}d_{mlj}+e_{jlm}d_{mlj})-\tfrac{1}{3}\,Au_{ij}, \tag{14}$$

$$D^2_{ij}=-\tfrac{1}{2}\sum_{l,m}\,(d_{ilm}e_{mlj}+d_{jlm}e_{mli})-\tfrac{1}{3}\,Au_{ij}\,. \tag{15}$$

Since $\overleftrightarrow{D}$ is traceless, the 3×3 matrix associated with each of the pseudodeviators has three eigenvalues $D_\alpha, D_\beta, D_\gamma$, such that

$$D_\alpha+D_\beta+D_\gamma=0. \tag{16}$$

As a function of $\overleftrightarrow{D}^1$ and $\overleftrightarrow{D}^2$ the two weight-2 third-rank tensors can be expressed as

$$d^{(2,1)}_{ijk}=\tfrac{1}{3}\textstyle\sum_l(2e_{ijl}D^1_{lk}+D^1_{il}e_{ljk})\,, \tag{17}$$

$$d^{(2,2)}_{ijk}=\tfrac{1}{3}\textstyle\sum_l\,(e_{ijl}D^2_{lk}+2D^2_{il}e_{ljk}). \tag{18}$$

We already mentioned that $A=0$ in the symmetric case. Since $e_{mlj}=-e_{lmj}$ it follows from Eq. (15) that $\overleftrightarrow{D}^2=0$ in that case. Both $\overleftrightarrow{D}^1$ and $\overleftrightarrow{D}^2$ are equal to zero in the fully symmetric case.

D. Septor

By making $\underline{d}$ fully symmetric and traceless one obtains the vector part, which has seven independent components. With the definitions

$$d^*_{ijk}=\tfrac{1}{6}\,(d_{ijk}+d_{jki}+d_{kij}+d_{kji}+d_{jik}+d_{ikj})\ , \tag{19}$$

$$V^*_i=\tfrac{1}{3}\,(V^1_i+V^2_i+V^3_i)\,, \tag{20}$$

it is found that

$$d^{(3)}_{ijk}=d^*_{ijk}-\tfrac{1}{5}\ V^*_i t_{jk}\ \ , \tag{21}$$

where t_{jk} equals 3 for $i=j=k$, $t_{jk}=1$ when two of the three indices ijk are the same, and $t_{jk}=0$ otherwise.

III. SCALAR INVARIANTS

The decomposition in irreducible parts leads immediately to the definition of several scalar invariants of $\underline{d}$ as, for instance, $|A|$, the magnitudes of the vectors $\vec{V}^1$, $\vec{V}^2$, and $\vec{V}^3$ (in the case of piezoelectricity $|V^1|$ is known[11] as the "hydrostatic piezoelectric coefficient") or the magnitudes of the six eigenvalues such as D^1_α. In the symmetric case (SHG and LEO) $\vec{V}^1$ and $\vec{V}^2$ vanish except for the polar (pyroelectric) classes and are both parallel to the polar axis in the case of the point group 2 and of all the point groups of higher symmetry. The specific magnitudes of $\vec{V}^1$ and $\vec{V}^2$ corresponding to the different point groups are listed in Table II.

We now consider in more detail the fully symmetric case, for which the decomposition of $\underline{d}$ is very simple:

$$\underline{d}=\underline{d}^{(1)}+\underline{d}^{(3)}\quad . \tag{22}$$

Therefore we can say that the optical nonlinearities are the superposition of two parts: a so-called vector part $\underline{d}^{(1)}$ and a septor part $\underline{d}^{(3)}$.

To the vector part we associate one scalar invariant, the magnitude V of $\vec{V}$. A general formula can be written for the orthorhombic, tetragonal, trigonal, and hexagonal systems,

$$V=|\,d_{311}+d_{322}+d_{333}\,|\ \ . \tag{23}$$

The septor part $\underline{d}^{(3)}$ has seven independent components in the case of the lowest symmetry (point group 1). Since the choice of $\vec{V}$ as an axis of the coordinate system takes only two degrees of freedom, it is possible to define six independent scalar invariants. For crystals of higher symmetry this number is lowered. Nevertheless there is always at least one scalar invariant S, and we define it as the square root of the sum of the squares of all the coefficients of the septor (see Table II).

Direct and simple use can be made of the scalar invariants V and S for interpreting previously reported[12,13] theoretical relations among the coefficients d_{ijk}. In a quantal treatment of optical nonlinearities in solids,[12] Robinson expands the perturbation potential $\mathcal{V}$ in terms of harmonic polynomials $r^l\,Y^m_J(\theta,\ \varphi)$[14]:

$$\mathcal{V}=\textstyle\sum_m\mathcal{V}^m_{33}r^3Y^m_3+\mathcal{V}^m_{31}r^3Y^m_1+\mathcal{V}^m_{11}rY^m_1\,, \tag{24}$$

and considers the assumption

$$\mathcal{V}^m_{31}=0\ \ , \tag{25}$$

so that $\mathcal{V}$ satisfies Laplace's equation. As a consequence, the Miller δ's[15] are found to be related by

$$\delta_{iii}+\delta_{ijj}+\delta_{ikk}=0. \tag{26}$$

The Cartesian third-rank tensor δ can be, like $\underline{d}$, decomposed in irreducible parts. Our analysis shows that Eq. (26) will be obtained every time the vector part is assumed to be zero, as for instance, by choosing $\mathcal{V}$ obeying Laplace's equa-

TABLE II. Scalar invariants associated to the vector part (symmetric case) and to the septor part (fully symmetric case) for the different classes.

Class	V^1	V^2	S
$\bar{4}3m$, 23			
$\bar{4}2m$			
222	0	0	$(\sqrt{6})\, d_{123}$
$6mm$, 6			
$4mm$, 4	$2d_{311}+d_{333}$	$2d_{131}+d_{333}$	$(\sqrt{\tfrac{2}{5}})\ (3d_{311}-d_{333})$
$\bar{6}m2$	0	0	$2d_{211}$
$\bar{6}$	0	0	$2[(d_{111})^2+(d_{211})^2]^{1/2}$
$\bar{4}$	0	0	$(\sqrt{6})[(d_{123})^2+(d_{311})^2]^{1/2}$
32	0	0	$2d_{111}$
$3m$	$2d_{311}+d_{333}$	$2d_{131}+d_{333}$	$[\tfrac{2}{5}(3d_{311}-d_{333})^2+4(d_{211})^2]^{1/2}$
3	$2d_{311}+d_{333}$	$2d_{131}+d_{333}$	$[\tfrac{2}{5}(3d_{311}-d_{333})^2+4(d_{211})^2+4(d_{111})^2]^{1/2}$
$mm2$	$d_{311}+d_{322}+d_{333}$	$d_{131}+d_{232}+d_{333}$	$[3(d_{311})^2+3(d_{322})^2+(d_{333})^2-\tfrac{3}{5}(V^*)^2]^{1/2}$

tion. Expanding $\mathcal{V}$ in terms of harmonic polynomials belongs to the same approach as considering the rotational invariance of $\underline{d}$: The $2J+1$ harmonic polynomials Y_J^m are a coordinate system for the subspace associated with the irreducible Cartesian tensor of weight J.[16] Equation (25) is therefore equivalent to $V=0$. If, on the other hand, one assumes that there is no septor part involved in the nonlinearities, the value of S for point groups $4mm$ and $6mm$ (see Table II) indicates

$$d_{333}=3d_{311}\ , \tag{27}$$

which is the result given by Robinson[12] for the sole perturbation in $\mathcal{V}$ being an internal field.

In another paper[13] and following a different approach, Robinson studied theoretically the optical nonlinearities in RX compounds which crystallize in one or both of the cubic (zinc-blende) and hexagonal (wurtzite) systems with nonlinear coefficients d^c_{ijk} and d^h_{ijk}, respectively. By ascribing the nonlinear polarizability to the undistorted RX_4 tetrahedral units, he obtained

$$-2d^h_{311}=-2d^h_{113}=d^h_{333}\ , \tag{28}$$

$$d^h_{333}=(2/\sqrt{3})\,d^c_{123}\ . \tag{29}$$

According to our analysis, Eq. (16) is just a statement of the fact that any vector part has been omitted ($V^1=0=V^2$) *a priori* by assuming the tetrahedron RX_4 regular. By contrast Eq. (29) cannot be derived from rotational invariance consideration; it gives the relation between the septor parts of the hexagonal and cubic structures built from the same regular unit.

It is interesting to note that any vector part has been implicitly neglected in Levine's calculations.[17] The validity of this assumption for the wurtzite structure will be discussed in Sec. IV.

IV. SPONTANEOUS POLARIZATION AND OPTICAL NONLINEARITIES

The analysis which has just been developed emphasizes a basic difference in the optical nonlinearities of nonpolar compared to polar crystals: Only the latter have a vector contribution to SHG and LEO. Since the polar crystals can also be defined by the existence of a spontaneous polarization $\vec{\mathcal{P}}_s$, parallel to $\vec{V}^1$ and $\vec{V}^2$, one is led to compare the magnitudes of the three vectors. First demonstrated by Miller[18] in barium titanate ($BaTiO_3$), correlations between spontaneous polarization and optical nonlinear properties have been studied experimentally and theoretically in several ferroelectric materials,[19-22] but no simple and general relation has been established. In order to find such a relation, the δ formulation[15] will be used and the cases of SHG and LEO will be considered successively. As a consequence of the relations between $d_{ijk}(2\omega,\omega,\omega)$ [or $d_{kji}(0,\omega,\omega)$] and δ_{ijk} [or ρ_{ijk}], the decomposition of the tensors $\underline{\delta}$ and $\underline{\rho}$ in irreducible parts is the same as for $\underline{d}$.

A. Second-Harmonic Generation

For all the materials studied until now Kleinman's relations are satisfied. We therefore assume the whole vector part of $\underline{\delta}$ described by

$$v=\left|\delta_{311}+\delta_{322}+\delta_{333}\right|\ . \tag{30}$$

The evaluation of v depends on the relative signs of the coefficients δ_{ijk}. Such signs have been determined in $LiNbO_3$, $LiTaO_3$, $BaTiO_3$, ZnO, $LiGaO_2$,[23] and $LiIO_3$.[24] By Maker fringe experiments[24] we found opposite signs for δ_{311} and δ_{333} in CdS but the same sign for δ_{311} and δ_{333} in $Ba_2NaNb_5O_{15}$ as theoretically predicted.[25]

Values of v and $\mathcal{P}_s$ corresponding to the materials for which a reliable complete set of data has been obtained are listed in Table III. As illustrated by Fig. 1, comparison of v and $\mathcal{P}_s$ indicates the vector part to be proportional to the spontaneous polarization

$$v = (0.10 \pm 0.03) \times 10^{-6} \mathcal{P}_s \text{ esu}, \qquad (31)$$

where $\mathcal{P}_s$ is in μ C cm^{-2}. A plot of the individual coefficients δ versus $\mathcal{P}_s$ leads to a considerably greater dispersion.[26] One can also note that the ratios $v/\mathcal{P}_s$ for $K_3Li_2Nb_5O_{15}$ and the ferroelectric phase of KDP agree with Eq. (31), provided the theoretically predicted relative signs are assumed[25,19] (see Fig. 1).

The wurtzite-type materials ZnO, CdS, and ZnS are not ferroelectric; their spontaneous polarizations cannot therefore be easily measured but have

TABLE III. Values of $v = |\delta_{311} + \delta_{322} + \delta_{333}|$ and of the spontaneous polarizations for polar materials. δ and v are in 10^{-6} esu units, $\mathcal{P}$ in μC cm^{-2}. Values inside parentheses have been computed assuming theoretical results on the relative signs of the coefficients δ. The value of δ_{321} for KDP in the paraelectric phase is 1.7×10^{-6} esu. Values of $\mathcal{P}_s$ inside brackets are estimated values.

N°	Material	Class	δ_{311}	δ_{322}	δ_{333}	v	$\mathcal{P}_s$
1	ZnO	6*mm*	−0.54 (Ref. 15)		1.80 (Ref. 15)	0.7 ±0.15	[6] (Ref. 27)
2	CdS	6*mm*	−0.82[a]		1.63[a]	0.02 ±0.15	[3] (Ref. 27)
			−1.5[b]		2.6[b]	0.4 ±1.2	
3	ZnS	6*mm*	±1.6[b]		3.1[b]		[2] (Ref. 27)
4	$LiIO_3$	6	2.85 (Ref. 24)		4.7	10.4 ±1	
5	$LiNbO_3$	3*m*	0.61 (Ref. 20)		5.9 (Ref. 20)	7.2 ±1.9	71[c]
			0.51[d]		3.9[d]	4.9 ±1.1	
6	$LiTaO_3$	3*m*	0.16 (Ref. 20)		2.7 (Ref. 20)	3.1 ± .4	50[c]
7	$BaTiO_3$	4*mm*	1.3 (Ref. 18)		0.56 (Ref. 18)	3.2 ± .2	26[e]
8	$K_3Li_2Nb_5O_{15}$	4*mm*	±0.8[f]		1.8[f]	(3.4 ± .5)	25[g]
9	$Ba_2NaNb_5O_{15}$	*mm*2	1.2[h]	1.4[h]	1.8[h]	4.4 ±0.5	40[c]
10	KDP	*mm*2	±2.1 (Ref. 19)	±1.4 (Ref. 19)	0 (Ref. 19)	(0.7 ± .4)	4.8[i]
11	$LiGaO_2$	*mm*2	0.06[j]	−0.14[j]	0.49[j]	0.4 ± .2	
12	$NaNO_2$	*mm*2	−1.85[k]	0.75[k]			6.4[l]
13	TGS	2	0 (Ref. 29)	±0.005 (Ref. 29)	0.013 (Ref. 29)		2.2[m]

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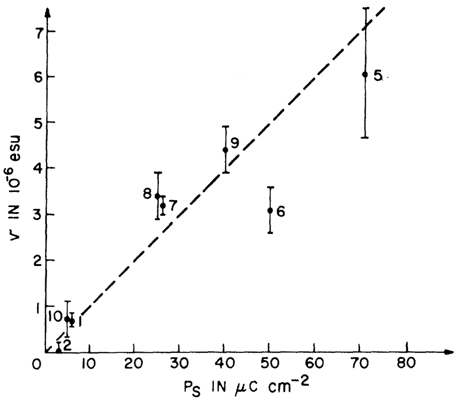

FIG. 1. Plot of the vector part $v = |\delta_{311} + \delta_{322} + \delta_{333}|$ in 10^{-6} esu as a function of the spontaneous polarization $\mathcal{P}_s$ in μC cm^{-2}. Values of v and $_s$ correspond, for each material, to the same temperature. Each material is indicated by its number, according to Table III. For $LiNbO_3$ (5) the average of the two values of v given on Table III has been plotted. The dashed line corresponds to the mean value of the ratio $v/\mathcal{P}_s$.

been estimated.[27] As a result, values of v deduced from Eq. (31) are in good agreement with experimental data. The higher value of $\mathcal{P}_s$ in ZnO compared to CdS and ZnS is consistent with the bigger distortion of the tetrahedron unit (the crystallographic ratio c/a equals 1.602 while for an ideal wurtzite structure $c/a = 1.633$).[28]

The magnitude of the vector part for triglycine sulfate (TGS) deduced from experimental data[29] (in any of the two alternatives for the relative sign of δ_{322} and δ_{333}) is 10 to 20 times lower than the value given by Eq. (31). Reasons for such a discrepancy can be found in the special character of the TGS structure, on the basis of a theoretical model explaining Eq. (31).[30]

B. Linear Electrooptic Effect

In an attempt to correlate the vector part of the LEO tensor $\underline{\rho}$ and the spontaneous polarization it is necessary to make first a distinction between clamped (or high-frequency or constant-strain) and unclamped (or low-frequency or constant-stress) phenomena. Since the latter depend greatly on piezoelectric and photoelastic properties, we will consider only the clamped quantities.

Despite that LEO has been known and studied for a long time, there are few materials for which the vector part and especially V^2 can be evaluated; they are listed on Table IV, where the values of the quantity

$$\Lambda_c^1 = |\rho^c_{311} + \rho^c_{322} + \rho^c_{333}| \qquad (32)$$

are also indicated. The comparison of Λ_c and $\mathcal{P}_s$ shows a linear dependence

$$\Lambda_c^1 = (4.5 \pm 1) \times 10^{-8}\, \mathcal{P}_s \text{ esu}, \qquad (33)$$

where $\mathcal{P}_s$ is in μC cm^{-2}.

V. DISCUSSION

The validity of phenomenological rules such as those given by Eqs. (31) and (33) does not rely only on the direct experimental confirmation, but also on the self-consistency of the conclusions to which they lead. In that respect it is worth noting the agreement between the values of $\mathcal{P}_s$ for $LiIO_3$ deduced from Eqs. (31) and (33): 105 ± 30 and 145 ± 20 μC cm^{-2}, respectively.

It is indeed possible to predict, from Eq. (31) or Eq. (33), values for nonlinear coefficients ($d_{333}^{NaNO_2} = 0.5\, d_{36}^{KDP}$) or for spontaneous polarizations ($\mathcal{P}_s^{LiGaO_2} = 4\,\mu$C cm^{-2}). But among all the consequences of a linear relation between the vector part of the optical nonlinearities and the spontaneous polarization, we would like to emphasize a particularly simple and useful one. It has been demonstrated by Abrahams *et al.*[31] that the spontaneous polarization is, in displacive ferroelectric crystals, proportional to the atomic displacement Δz. One can therefore, for this particular group of crystals, relate the SHG coefficients to the atomic positions

TABLE IV. Values, for LEO, of the clamped vector part $\Lambda_c^1 = |\rho^c_{311} + \rho^c_{322} + \rho^c_{333}|$ in 10^{-8} esu, at the wavelength 6327 Å. For wurtzite materials calculated values of Λ_c^1 using Eq. (33) and estimated $\mathcal{P}_s$ are indicated.

Material	Class	Λ_c^1	$\mathcal{P}_s$	$\Lambda_c^1/\mathcal{P}_s$	Λ_c^1 (calc)
ZnO	6*mm*	6 ± 15[a]	[6] (Ref. 27)	[1]	26
CdS	6*mm*	4 ± 15[a]	[3] (Ref. 27)	[1.5]	14
ZnS	6*mm*	0 ± 15[a]	[2] (Ref. 27)	[0]	9
$LiIO_3$	6	660 ± 100[b]			
$LiNbO_3$	3*m*	320 ± 40[c,d]	71[e]	4.5	
$LiTaO_3$	3*m*	235 ± 30[f]	50[e]	4.7	
$BaTiO_3$	4*mm*	103 ± 15[g]	26[h]	4.0	

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in the crystallographic structure[32] by the linear equation

$$\nu = (24 \pm 5)\times 10^{8}\,\Delta z \text{ esu.} \tag{34}$$

Little attention has been paid so far to the septor part of $\underline{\delta}$ or $\underline{\rho}$ which is correlated to an "octupole" moment. The physical interpretation is not as obvious as for the vector part but use can be made of S for studying phase transformations. As an example, let us consider the transition at low temperature, of KDP from a paraelectric phase ($\bar{4}2m$) to a ferroelectric one ($mm2$). Above the Curie temperature the SHG properties of the tetragonal structure are completely described by the septor scalar invariant σ_t (in the δ formulation). On the other hand, both v_o and σ_o are allowed by the orthorhombic structure. The vector part v_o has been shown to be related to the spontaneous polarization $\mathcal{P}_s$ while the septor parts σ_o and σ_t are experimentally the same (see Tables II and III). All the changes in SHG properties of KDP at the phase transformation can therefore be explained in terms of a vector contribution in the ferroelectric phase.

VI. CONCLUSION

The optical nonlinearities of crystals have been analyzed from a new and fundamental point of view which differentiates polar from nonpolar materials on the basis of a vector contribution to the phenomena described by a third-rank tensor. The decomposition into vector and septor parts allows a general explanation of previously reported theoretical results and strongly suggests simple relations between different physical properties. The so-called vector part has been shown to be proportional to the spontaneous polarization and new relations among optical nonlinear coefficients have been consequently established.

Note added in manuscript. Discussions with Dr. J. A. Giordmaine, Dr. R. C. Miller, and Dr. D. A. Kleinman drew our attention to the fact that information about the signs of the nonlinear coefficients can be deduced from the results reported above. For both SHG and LEO, there is a proportionality between the spontaneous polarization $\vec{\mathcal{P}}_s$ and the vector $\vec{V}^1$. The sign of the scalar product $\vec{V}^1 \cdot \vec{\mathcal{P}}_s$ is therefore the same for all the materials. This has been demonstrated in the case of SHG by Miller and Nordland,[33] who found $\vec{V}^1 \cdot \mathcal{P}_s < 0$, for $LiNbO_3$, $LiTaO_3$, $BaTiO_3$, ZnO, and also for $Ba_2NaNb_5O_{15}$.[34] We deduce that d_{311} and d_{333} are negative for $LiIO_3$ while d_{311} is negative and d_{322} positive in the ferroelectric phase of KDP. The experiments performed in $LiNbO_3$ by Hulme *et al.*[35] show that r_{33} is positive. Since $\rho_{kji}(0,\omega,\omega)$ and $r_{ik}(\omega)$ have opposite signs, $\vec{V}^1 \cdot \mathcal{P}_s$ is negative for LEO.

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Ultrasonic Beam Mixing as a Measure of the Nonlinear Parameters of Fused Silica and Single-Crystal NaCl[†][*]

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The mixing action of two crossed ultrasonic beams has been studied. The theoretical treatment of Taylor and Rollins is extended to include the all-pure-mode cases for the prosess

$$L(\omega_1) - T\begin{Bmatrix}\omega_2\\ \omega_1-\omega_2\end{Bmatrix} \to T\begin{Bmatrix}\omega_1-\omega_2\\ \omega_2\end{Bmatrix}$$

in cubic single crystals. Five such cases exist in cubic crystals; two in the (001) mixing plane and with L (ω_1) propagated in either of two fixed directions [100] and [110]; and the other three in the $(1\bar{1}0)$ mixing plane and with L (ω_1) propagated in any of three fixed directions [110], [111], and [001]. The transverse waves are polarized normal to the mixing plane in all five cases and propagate in directions within the plane corresponding to the selection rules on frequency and propagation vector. The conversion efficiency was measured over a range of input frequency ratios, $a=\omega_2/\omega_1$ for the two independent transverse-polarization states for the above process in fused silica and for the two pure-mode cases in the (001) plane in NaCl. A comparison technique using the interchange equivalence of $T(\omega_2)$ and $T(\omega_1-\omega_2)$ effectively eliminated the transducer-bond efficiencies. These measurements were used to determine two of the three independent third-order elastic constants of fused silica. In the case of NaCl, the two ratios of linear combinations of second- and third-order elastic constants corresponding to the two (001)-plane pure-mode cases were determined. The above comparison technique was not applied to the other three pure-mode cases because the transverse anisotropy in the $(1\bar{1}0)$ plane leads to refractive effects on the transverse beams that render the technique inapplicable.

I. INTRODUCTION

In this investigation we explore the mixing action in the crossing of ultrasonic beams and the measurement of the conversion efficiency to determine parameters characterizing the nonlinearity of materials. When two large-amplitude ultrasonic waves intersect in a solid at an angle appropriate to the particular ratio of their frequencies, a third ultrasonic wave generally radiates from their common volume of intersection. The third wave propagates in still another direction so that there is a conservation relation among the three propagation vectors involved. The third wave has either the sum or difference frequency of the two primary waves depending on the particular mode combination.