

# Quadratic Electrostrictive Effects in LiF, NaF, NaCl, NaBr, KCl, KBr, KI, RbCl, RbBr and RbI

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Quadratic electrostrictive effects of both longitudinal and transverse type have been measured on LiF, NaF, NaCl, NaBr, KCl, KBr, KI, RbCl, RbBr and RbI single crystals with an improved frequency-modulation technique with a 100 MHz oscillator. The three independent tensor components  $d_{1111}$ ,  $d_{1122}$ ,  $d_{1212}$ , defined as  $d_{ijkl} = \frac{1}{2} \partial^2 \varepsilon_{ij} / \partial E_k \partial E_l$ , have been determined for all these crystals.  $\varepsilon_{ij}$  are the components of the strain tensor and  $E_k$  the components of the electric field vector. All longitudinal components  $d_{1111}$  and all 'shear' components  $d_{1212}$  are negative; all transverse components  $d_{1122}$  are positive. The electric field causes a volume contraction in these crystals. The theoretical values for  $d_{1111}$  as derived by Grindlay & Wong [*Canad. J. Phys.* (1969), 47, 1563–1571] agree well with the experimental data. Larger discrepancies are found between the predicted and observed behaviour of  $d_{1122}$  and  $d_{1212}$ . Within the isotypic crystal group of alkali halides of rocksalt type the components  $d_{1111}$  show a positive correlation with the dielectric constants. The appreciable electrostrictive contribution to the total electro-optical effect is discussed.

## Introduction

Quadratic electrostrictive effects were observed first in Rochelle salt by Mueller (1940). Other ferroelectric materials like BaTiO<sub>3</sub> ceramics have been investigated by Mason (1948) who also gave a phenomenological description of the effect. Since then a great number of electrostrictive data of ferroelectric crystals have become available (*Landolt-Börnstein*, 1969). The situation in the field of nonferroelectric crystals is quite different owing to the extremely small effects in such crystals. Zheludev & Fotchenkov (1958) reported measurements on NaCl and on a z-cut quartz crystal. Gundjian (1965) determined the quadratic electrostriction in germanium. Besson & Mesnage (1970) worked on quartz and on different synthetics. Burkard & Känzig (1975; Burkard, Känzig & Rossinelli, 1976) have investigated the transverse quadratic electrostriction on pure KCl and KBr and partially substituted alkali halides.

Recently, new interest in such effects arose from different aspects of nonlinear optics such as self-focusing phenomena, stimulated Brillouin scattering, and quadratic electro-optic effects. In all these fields the quadratic electrostrictive coefficients are directly related to the material properties involved. Mainly for the further elucidation of these properties we undertook to improve the experimental methods for measuring the smallest amount of mechanical deformation expected in quadratic electrostrictive effects in centrosymmetric crystals. Our first results obtained from a series of alkali halide crystals of rocksalt type are presented here.

## Phenomenological description

Quadratic electrostrictive coefficients are defined as third-order derivatives of the thermodynamic potential

functions. Introducing the second-order terms of the expansion of the thermodynamic potential functions the following relations are obtained for both isothermal and isentropic conditions:

$$\begin{aligned} d_{ijmq} &= \frac{1}{2} \left( \frac{\partial^2 \varepsilon_{ij}}{\partial E_m \partial E_q} \right)_\sigma = \frac{1}{2} \left( \frac{\partial^2 D_m}{\partial \sigma_{ij} \partial E_q} \right) = \frac{1}{2} \left( \frac{\partial^2 D_q}{\partial \sigma_{ij} \partial E_m} \right) \\ b_{ijmq} &= \frac{1}{2} \left( \frac{\partial^2 \varepsilon_{ij}}{\partial D_m \partial D_q} \right)_\sigma = -\frac{1}{2} \left( \frac{\partial^2 E_m}{\partial \sigma_{ij} \partial D_q} \right) = -\frac{1}{2} \left( \frac{\partial^2 E_q}{\partial \sigma_{ij} \partial D_m} \right) \\ f_{ijmq} &= \frac{1}{2} \left( \frac{\partial^2 \sigma_{ij}}{\partial E_m \partial E_q} \right)_\varepsilon = -\frac{1}{2} \left( \frac{\partial^2 D_m}{\partial \varepsilon_{ij} \partial E_q} \right) = -\frac{1}{2} \left( \frac{\partial^2 D_q}{\partial \varepsilon_{ij} \partial E_m} \right) \\ h_{ijmq} &= \frac{1}{2} \left( \frac{\partial^2 \sigma_{ij}}{\partial D_m \partial D_q} \right)_\varepsilon = \frac{1}{2} \left( \frac{\partial^2 E_m}{\partial \varepsilon_{ij} \partial D_q} \right) = \frac{1}{2} \left( \frac{\partial^2 E_q}{\partial \varepsilon_{ij} \partial D_m} \right). \end{aligned}$$

The corresponding tensor relations are

$$\begin{aligned} \varepsilon_{ij} &= d_{ijmq} E_m E_q, & \sigma_{ij} &= f_{ijmq} E_m E_q, \\ D_m &= 2d_{ijmq} \sigma_{ij} E_q, & D_m &= -2f_{ijmq} \varepsilon_{ij} E_q, \\ \varepsilon_{ij} &= b_{ijmq} D_m D_q, & \sigma_{ij} &= h_{ijmq} D_m D_q, \\ E_m &= -2b_{ijmq} \sigma_{ij} D_q, & E_m &= 2h_{ijmq} \varepsilon_{ij} D_q. * \end{aligned}$$

The symbols  $\varepsilon_{ij}$ ,  $\sigma_{ij}$ ,  $E_i$ ,  $D_i$ ,  $d_{ijkl}$ ,  $b_{ijkl}$ ,  $f_{ijkl}$ ,  $h_{ijkl}$  are respectively the components of the quantities: strain tensor, stress tensor, electric field vector, dielectric displacement vector, tensors of the quadratic electrostrictive effects.

All four tensors [ $d_{ijkl}$ ], [ $b_{ijkl}$ ], [ $f_{ijkl}$ ] and [ $h_{ijkl}$ ] possess the symmetry properties:

$$d_{ijkl} = d_{jikl} = d_{jilk} = d_{ijlk},$$

owing to the corresponding symmetry properties of the other tensors involved and by virtue of the thermodynamic relations. Concerning the type of

\* Concerning summation, the Einstein convention is used.

independent components resulting from crystal symmetry, these tensors behave like the elasto-optic tensor.

Between the four tensors exist the relations:

$$\begin{aligned}
 d_{ijmq}^{\sigma} &= s_{ijkl}^E f_{klmq}^{\sigma} & f_{ijmq}^{\epsilon} &= c_{ijkl}^E d_{klmq}^{\sigma} & (1) \\
 b_{ijmq}^{\sigma} &= s_{ijkl}^D h_{klmq}^{\epsilon} & h_{ijmq}^{\epsilon} &= c_{ijkl}^D b_{klmq}^{\sigma} \\
 b_{ijrs}^{\sigma} &= a_{mr}^{\sigma} a_{qs}^{\sigma} d_{ijmq}^{\sigma} & d_{ijrs}^{\sigma} &= \epsilon_{mr}^{\sigma} \epsilon_{qs}^{\sigma} b_{ijmq}^{\sigma} \\
 h_{ijrs}^{\epsilon} &= a_{mr}^{\epsilon} a_{qs}^{\epsilon} f_{ijmq}^{\epsilon} & f_{ijrs}^{\epsilon} &= \epsilon_{mr}^{\epsilon} \epsilon_{qs}^{\epsilon} h_{ijmq}^{\epsilon} \\
 d_{ijmq}^{\sigma} &= s_{ijkl}^E \epsilon_{rm}^{\epsilon} \epsilon_{sq}^{\epsilon} h_{klrs}^{\epsilon} \\
 b_{ijmq}^{\sigma} &= s_{ijkl}^D a_{rm}^{\epsilon} a_{sq}^{\epsilon} f_{klrs}^{\epsilon} \\
 f_{ijmq}^{\epsilon} &= c_{ijkl}^D \epsilon_{rm}^{\epsilon} \epsilon_{sq}^{\epsilon} b_{klrs}^{\sigma} \\
 h_{ijmq}^{\epsilon} &= c_{ijkl}^E a_{rm}^{\epsilon} a_{sq}^{\epsilon} d_{klrs}^{\sigma} .
 \end{aligned}$$

The symbols introduced are  $[\epsilon_{ij}]$  dielectric tensor,  $[a_{ij}]$  polarization tensor, defined by  $[a_{ij}] = [\epsilon_{ij}]^{-1}$ ,  $[s_{ijkl}]$  elastic compliance tensor and  $[c_{ijkl}]$  elastic stiffness tensor.

### Experimental procedure

Specimen and auxiliary crystal, both plated, are cemented onto the electrode plates of a capacitor unit which is the frequency-controlling element of a 100 MHz oscillator. An alternating electric field with frequency  $\nu$  ( $\nu$  between 60 and 160 Hz) applied to the specimen produces a quadratic electrostrictive deformation vibrating with frequency  $2\nu$ , if the crystal possesses inversion symmetry. These periodic deformations change the distance between the capacitor plates and therefore cause a frequency modulation of the oscillator. The auxiliary crystal, here a (111)-cut  $\text{NaBrO}_3$  crystal, exhibits a linear electrostrictive effect. Thus if an alternating electric field with frequency  $2\nu$  is applied to this crystal, mechanical deformations with frequency  $2\nu$  are also generated in the auxiliary crystal. After adjusting the phase of the deformations in the auxiliary crystal to be opposite to the phase of the deformations in the specimen, it is possible to keep the separation of the capacitor plates constant by choosing a proper ratio of the two voltages applied. In the case of zero compensation, the amplitude of the demodulated signal of the 100 MHz oscillator will disappear. The voltage applied to the auxiliary crystal gives a direct measure of the amplitude of deformation in the specimen if the corresponding linear electrostrictive coefficient is known. In our case this coefficient is of magnitude  $1.40 \times 10^{-12} \text{ m V}^{-1}$ .

Additionally, we employed a LOCK-IN technique at the frequency  $2\nu$  and achieved an essential improvement in the arrangement. The reproducible sensitivity obtained corresponds to a change in length  $\Delta L = 1 \times 10^{-13} \text{ m}$  under optimal conditions of specimen form and size, shielding of all electrical leads and utmost measures for damping any mechanical vibrations from outside and inside the capacitor system. The deformations generated in the specimens ranged

between  $10^{-11}$  and  $10^{-12} \text{ m}$  when maximum electric fields of strength  $20 \text{ kV cm}^{-1}$  were used. The arrangement of the specimen and auxiliary crystals for the measurement of longitudinal effects is illustrated in Fig. 1. In the case of longitudinal effects (electric field vector and observed mechanical displacement parallel) we used disc-like specimens with diameters of 10 to 20 mm and thicknesses of 1 to 4 mm. For the measurement of transverse effects (electric field vector and observed mechanical displacement perpendicular) we prepared rectangular parallelepipeds  $ca 6 \times 10 \times 10 \text{ mm}$ . The crystals were melt-grown and of high optical quality. The electric field was applied in the direction of the smallest dimension.

The equations combining the tensor components and the observed deformations are

$$d'_{1111} = \frac{\Delta L'_1}{L'_1 E_1^2} + \frac{1}{2} \epsilon_0 \epsilon'_{11} s'_{1111} = L'_1 \frac{\Delta L'_1}{U^2} + \frac{1}{2} \epsilon_0 \epsilon'_{11} s'_{1111}$$

for longitudinal effects and

$$d'_{1122} = \frac{\Delta L'_1}{L'_1 E_2^2} + \frac{1}{2} \epsilon_0 \epsilon'_{22} s'_{1122} = \frac{L_2'^2}{L'_1} \frac{\Delta L'_1}{U^2} + \frac{1}{2} \epsilon_0 \epsilon'_{22} s'_{1122}$$

for transverse effects.

The primed symbols are referred to an arbitrary Cartesian reference system with the axes  $\mathbf{e}'_i = u_{ij} \mathbf{e}_j$ , where the unit vectors  $\mathbf{e}_i$  are chosen parallel to the cubic crystal axes.  $L'_1$  is the thickness of the specimen in the direction  $\mathbf{e}'_1$ , and  $\Delta L'_1$  the absolute change of this dimension after application of the electric field. The second term of the equations gives the deformation resulting from the attractive forces between the metallized electrodes of the specimen.

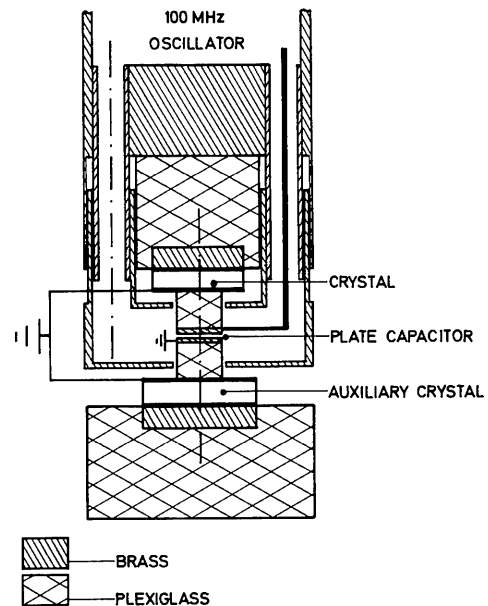


Fig. 1. Arrangement of the specimen and auxiliary crystals for the measurement of longitudinal effects.

In crystals of point group symmetry  $m3m$ , in which the alkali halides crystallize, only three independent components  $d_{1111}$ ,  $d_{1122}$ , and  $d_{1212}$  exist. For the evaluation of these components we performed measurements in directions of electric field and displacements as given in Table 1.

Table 1. Directions  $\mathbf{e}'_i$  of electric field  $\mathbf{E}$  and  $\mathbf{e}'_i$  of observed deformation  $\Delta L'_i/L'_i$

$\mathbf{e}'_i \parallel$	$\mathbf{E} \parallel$	$d_{ijkl}$ involved
$[100]'$	$[100]'$	$d'_{1111} = d_{1111}$
$[110]'$	$[110]'$	$d'_{1111} = \frac{1}{2}d_{1111} + \frac{1}{2}d_{1122} + d_{1212}$
$[111]'$	$[111]'$	$d'_{1111} = \frac{1}{3}d_{1111} + \frac{2}{3}d_{1122} + \frac{4}{3}d_{1212}$
$[100]'$	$[010]'$	$d'_{1122} = d_{1122}$
$[110]'$	$[\bar{1}10]'$	$d'_{1122} = \frac{1}{2}d_{1111} + \frac{1}{2}d_{1122} - d_{1212}$

The observed values were treated by a least-squares method. The results for the components  $d_{ijkl}$  together with the limits for the probable errors are given in Table 2.

Table 2. Quadratic electrostrictive coefficients  $d_{ijkl}$  of alkali halides at 20°C

Units are  $10^{-20} \text{ m}^2 \text{ V}^{-2}$ . The limits for the probable relative errors are  $d_{1111}$  15%,  $d_{1122}$  25%,  $d_{1212}$  15%.

	$d_{1111}$	$d_{1122}$	$d_{1212}$
LiF	-0.72	+0.25	-0.40
NaF	-0.66	+0.25	-0.43
NaCl	-0.67	+0.24	-0.38
NaBr	-1.57	+0.59	-1.01
KCl	-0.56	+0.18	-0.55
KBr	-0.84	+0.32	-0.65
KI	-1.37	+0.56	-0.64
RbCl	-0.81	+0.26	-0.51
RbBr	-1.00	+0.40	-0.59
RbI	-1.42	+0.50	-1.03

## Discussion

### 1. Comparison with earlier data

Experimental values for NaCl have been determined by Zheludev & Fotchenkov (1958) and Zhedulev (1971) who found  $d_{1111} = +0.3$ ,  $d_{1122} = -0.15$ ,  $d_{1212} = +0.05 \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$ . Burkard & Känzig (1975) and Burkard, Känzig & Rossinelli (1976) have investigated the transverse quadratic electrostriction of pure KCl and KBr and partially substituted KCl:OH<sup>-</sup>, KCl:Li<sup>+</sup>, NaBr:F<sup>-</sup>, RbCl:Ag<sup>+</sup>, RbBr:Ag<sup>+</sup> and KBr:Li<sup>+</sup> at low temperatures. Their results for pure crystals at 4.2 K are:  $d_{1122}(\text{KCl}) = -0.15$ ,  $d_{1122}(\text{KBr}) = -0.26 \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$ . The discrepancies between our values and those of Zheludev & Fotchenkov are much higher than the experimental errors would allow. The signs of all three constants differ, and our values are about twice theirs. The signs of Burkard &

Table 3. Pressure derivatives  $\frac{1}{\epsilon_{11}} \frac{\partial \epsilon_{11}}{\partial p}$  of dielectric constants  $\epsilon_{11}$  of alkali halides in units of  $10^{-10} \text{ N}^{-1} \text{ m}^2$

	Present work	Experimental values
LiF	-0.55	-0.509*
NaF	-0.71	-0.540*
NaCl	-0.73	-1.039*
NaBr	-1.38	-1.270*
KCl	-0.94	-1.101*
KBr	-0.93	-1.249*
KI	-1.15	-1.26†
RbCl	-1.33	-1.14†
RbBr	-0.93	-1.26†
RbI	-1.92	-1.32†

\* Fontanella, Andeen & Schuele (1972).

† Jones (1967).

Känzig's values also differ from ours, but the absolute values agree well within the limits of error.\*

In Table 3 experimental values for the pressure derivatives of the dielectric constants  $\epsilon_{11}$  measured by Fontanella, Andeen & Schuele (1972) and Jones (1967), are compared with values which were calculated from our  $d_{ijkl}$  by

$$\frac{1}{\epsilon_{11}} \frac{\partial \epsilon_{11}}{\partial p} = \frac{2}{\epsilon_{11}} \sum_{i=1}^3 d_{11ii} = \frac{2}{\epsilon_{11}} (d_{1111} + 2d_{1122}),$$

where  $p$  is the pressure.

The errors for this expression are remarkably higher than for the individual constants because of the opposite signs of  $d_{1111}$  and  $d_{1122}$ . Here, good agreement between both sets of values is observed.

Grindlay & Wong (1969) have derived equations for the temperature-independent quadratic electrostrictive coefficients  $f_{ijkl}$  of a finite non-piezoelectric ionic crystal composed of nonpolarizable point charges, on an arbitrary basis. The values calculated from their

\* It should be mentioned that only small differences in the quasistatic values between 4.2 and 293 K are expected owing to the small change in density, less than 2% within this temperature range, of the crystals under investigation.

Table 4. Quadratic electrostrictive coefficients  $f_{ijkl}$  derived from Grindlay & Wong's (1969) formula:

$$Q_{ijkl} = -2f_{klij}$$

In brackets the values from this work are given. Units are  $10^{-10} \text{ N V}^{-2}$ .

	$f_{1111}$	$f_{1122}$	$f_{1212}$
LiF	-6.71 (-5.77)	+0.47 (+5.82)	+0.13 (-5.08)
NaF	-2.69 (-5.19)	+0.35 (+1.43)	+0.17 (-2.41)
NaCl	-3.07 (-2.67)	+0.38 (+0.62)	+0.18 (-0.97)
NaBr	-4.52 (-4.95)	+0.37 (+1.24)	+0.14 (-2.00)
KCl	-2.40 (-2.04)	+0.30 (+0.47)	+0.14 (-0.70)
KBr	-2.42 (-2.56)	+0.30 (+0.82)	+0.14 (-0.66)
KI	-3.29 (-3.28)	+0.29 (+1.17)	+0.12 (-0.49)
RbCl	-3.16 (-2.64)	+0.30 (+0.61)	+0.12 (-0.48)
RbBr	-3.15 (-2.80)	+0.29 (+0.99)	+0.12 (-0.45)
RbI	-3.47 (-3.30)	+0.28 (+0.95)	+0.11 (-0.58)

formula are listed in Table 4 together with the values which are obtained from our  $d_{ijkl}$  with equation (1). The agreement in the longitudinal coefficients  $f_{1111}$  is excellent, but certain deviations appear in the transverse coefficients  $f_{1122}$ . The largest discrepancy is found with  $f_{1212}$ , where the theoretical treatment predicts a different sign even.

These differences show that the assumption of non-polarizable point charges in the calculations of Grindlay & Wong (1969) is not sufficient to explain the complete electrostrictive behaviour of alkali halides.

## 2. Electrostrictive behaviour of the isotypic group and relations with other properties

The general electrostrictive behaviour of the isotypic group of alkali halides of rocksalt type may be described as follows. (I) All components  $d_{ijkl}$  have the same order of magnitude:  $10^{-20} \text{ m}^2 \text{ V}^{-2}$ , (II) All components  $d_{1111}$  and  $d_{1212}$  possess negative signs, all components  $d_{1122}$  positive signs. The crystals contract in the field direction and expand in directions perpendicular to the electric field. (III) The volume changes  $\Delta V/V$  introduced by an electric field are always negative. (IV) The sign of  $d_{2211}/d_{1111}$ , which expresses the ratio of transverse to longitudinal deformations caused by an electric field parallel to  $[100]$ , corresponds to the sign of  $s_{2211}/s_{1111}$ , the ratio of transverse to longitudinal elastic deformations excited by a uniaxial pressure parallel to  $[100]$ . Therefore an appreciable part of the transverse electrostrictive effect is due to elastic transverse coupling. (V) There exists a correlation between dielectric constants and the longitudinal and transverse effects in the  $[d_{ijkl}]$  and  $[f_{ijkl}]$  tensors. The minima of these properties are observed in KCl which possesses the smallest packing density.

A trend to higher values of  $d_{1111}$  with increasing anion size is also observed within the groups of sodium, potassium, and rubidium halides. The dielectric constants behave similarly.

## 3. The contribution of the quadratic electrostriction in electro-optic effects (Kerr effect and stimulated Brillouin scattering)

The quadratic electro-optic effect (Kerr effect) is

represented by the following relation between electric field  $\mathbf{E}$  and the change of polarization constants  $a_{ij}$ :

$$\Delta a_{ij} = g_{ijkl} E_k E_l + q_{ijkl} \sigma_{kl};$$

$g_{ijkl}$ ,  $q_{ijkl}$  and  $\sigma_{kl}$  are respectively the components of the total quadratic electro-optic tensor, the piezo-optic tensor and the mechanical stress tensor.  $g_{ijkl}$  consists of two components:

$$g_{ijkl} = \bar{g}_{ijkl} + p_{ijmn} d_{mnkl}.$$

The first is the true electro-optic effect, the second the electrostrictively induced elasto-optic effect.  $p_{ijkl}$  are the components of the elasto-optic tensor. As the complete tensors involved are now available we are able to evaluate the electrostrictive-elasto-optic contribution (see below). But quadratic electrostriction still has one further influence, if the usual experimental procedure for the determination of electro-optic effects is employed, namely the measurement of changes in the optical path differences,  $\Delta S$ , introduced by an applied electric field. The relation between  $S$ , the path length  $L$ , and the indices of refraction  $n'$  and  $n''$  of two interfering waves is:

$$\Delta S = \Delta[L(n' - n'')] = L[\Delta(n' - n'')] + (n' - n'')\Delta L.$$

The first term represents the change in optical constants due to the electric field, which is the intrinsic electro-optic effect. This term also includes the piezo-optic contribution originating from the attraction of the electrode plates. The second term results from the geometrical change of the path length, and consists of two parts: the electrostriction effect and the elastic deformation also caused by the attraction of the electrode plates. With certain arrangements employing auxiliary electrodes it is possible to suppress the piezo-optic and elastic contributions. But with quasi-static measurements it is by no means possible to eliminate the electrostrictive effect, except in the case of optical isotropy, as in cubic crystals, or in the direction of an optical axis.

For the so-called 'absolute' measurements, interference effects of a wave travelling in a vacuum with only one wave travelling through the crystals, are observed. In this case  $n''$  is the vacuum index of re-

Table 5. Electro-optic properties of alkali halides

'Relative' effects  $g_{1111} - g_{1122}$  and  $g_{1212}$  (Haussühl & Hesse, 1968). True effects  $\bar{g}_{1111} - \bar{g}_{1122}$  and  $\bar{g}_{1212}$ . Electrostrictive contributions  $p_{11mn}d_{mn11} - p_{11mn}d_{mn22}$  and  $p_{12mn}d_{mn12}$  [ $p_{ijkl} = q_{ijmn}c_{mnkl}$ ;  $q_{ijkl}$  after Leibsle (1960),  $c_{ijkl}$  after Spangenberg & Haussühl (1957)]. Units are  $10^{-22} \text{ m}^2 \text{ V}^{-2}$ .

	$g_{1111} - g_{1122}$	$g_{1212}$	$\bar{g}_{1111} - \bar{g}_{1122}$	$\bar{g}_{1212}$	$p_{11mn}d_{mn11} - p_{11mn}d_{mn22}$	$p_{12mn}d_{mn12}$
LiF	-3.53	-0.70	-13.2	-3.54	+9.67	+2.84
NaF	-1.15	-0.63	-10.3	-2.69	+9.15	+2.06
NaCl	+1.30	-1.67	-3.07	-2.51	+4.37	+0.84
NaBr	+2.51	-2.93	+10.1	-3.74	-7.59	+0.81
KCl	+1.03	+1.46	+5.69	-1.51	-4.66	+2.97
KBr	+1.03	+1.00	+6.71	-1.60	-5.68	+2.60
KI	+1.26	-0.82	+8.79	-2.10	-7.53	+1.28
RbCl	-0.11	+3.90	-13.1	+0.13	+12.99	+3.77
RbBr	-0.20	+3.52	-16.9	-0.37	+16.70	+3.89
RbI	-0.74	+2.15	-18.8	-2.38	+18.06	+4.53

fraction (=1). The electrostrictive contribution will therefore never vanish in the case of 'absolute' measurements which are necessary for a complete determination of the quadratic electro-optic tensor. As an example we consider now the situation in LiF, where experimental values for the constants  $g'_{1111} = -25.6 \times 10^{-22}$  and  $g'_{1122} = -21.4 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$  have been determined by Haussühl & Walda (1971). The primed values still contain the piezo-optic contribution, the change of optical path length induced by attraction of the electrodes and that introduced by electrostriction. The last contribution is the largest:  $7.27 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$ . This indicates that the electrostrictive change of geometrical path length contributes substantially to the total quadratic electro-optical effects and cannot be ignored. Now we calculate these three contributions and obtain corrected values  $g_{1111} = -18.1 \times 10^{-22}$  and  $g_{1122} = -13.3 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$ . From our values of  $d_{ijkl}$  and the already known elasto-optic constants  $p_{ijkl} = q_{ijmn} c_{mnkl}$  (Leibssle, 1960; Spangenberg & Haussühl, 1957) we derive the electrostrictive-elasto-optical contributions  $p_{11mn} d_{mn11} = g_{1111} - \bar{g}_{1111} = 3.64 \times 10^{-22}$  and  $p_{11mn} d_{mn22} = g_{1122} - \bar{g}_{1122} = 6.06 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$ . We recognize that the electrostrictive-elasto-optic contribution possesses the same order of magnitude as the true effect  $\bar{g}_{ijkl}$ , and exhibits an opposite sign.

In the case of 'relative' measurements, where the optical path difference between two waves travelling through the crystal in the same direction is observed, the electrostrictive change of path length cancels, but not the electrostrictive-elasto-optic contribution, as shown in Table 5. Also in this case the electrostrictive-elasto-optical effects play an important role.

These results are supported in some respect by Larionov & Malkin's (1974) theoretical work. On the basis of the shell model, applied to NaF and NaI, these authors found that the sign of the Kerr effect in NaF and NaI is governed by the electrostrictive-elasto-optic contribution.

As a last remark we would like to emphasize the fundamental importance of quadratic electrostrictive

properties in stimulated Brillouin scattering experiments. The methods of measuring the quadratic electrostriction as outlined in this paper should allow further systematic investigations which also may lead to a better understanding of the crystal properties in connexion with stimulated Brillouin scattering.

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