

Magnitude and nature of the quadratic electro-optic effect in potassium dihydrogen phosphate and ammonium dihydrogen phosphate crystals

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Measurements of the magnitude and the sign of certain quadratic electro-optic coefficients of potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) were made with an actively stabilized Michelson interferometer. The results obtained for these coefficients are, in units of $10^{-20} \text{ m}^2 \text{ V}^{-2}$ (as opposed to literature values of order $10^{-18} \text{ m}^2 \text{ V}^{-2}$), as follows: (KDP) $g_{xxxx} = -3.4 \pm 0.5$, $g_{yyxx} = -0.2 \pm 0.4$, and $g_{zzxx} = -0.7 \pm 0.4$; (ADP) $g_{xxxx} = -7.4 \pm 1.0$, $g_{yyxx} = -1.7 \pm 0.9$, and $g_{zzxx} = -1.4 \pm 0.9$. The quadratic Faust–Henry coefficient describing the lattice and the electronic contributions to the quadratic electro-optic effect in KDP and ADP is estimated from our results. These show that the nonlinear susceptibility responsible for the quadratic electro-optic effect in these crystals is due mainly to nonlinear interactions of the low-frequency electric field with the crystal lattice. © 2001 Optical Society of America

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1. INTRODUCTION

The electro-optic effect manifests itself as a change in the refractive index of a medium to which a static or a low-frequency electric field is applied. It not only finds extensive use in a variety of technological applications but can also be related to other nonlinear phenomena such as Brillouin and Raman scattering and wave mixing.¹ Thus the study of electro-optic properties is also of importance in obtaining an insight into the nature of nonlinear phenomena.

The electro-optic coefficients are traditionally defined in terms of changes in the impermeability B_{ij} induced in a crystal by an electric field \mathbf{E} :

$$\Delta B_{ij} = r_{ijk} E_k + g_{ijkl} E_k E_l + \dots, \quad (1)$$

where r_{ijk} and g_{ijkl} are the linear and the quadratic electro-optic coefficients, respectively. Discussions and investigations of the electro-optic properties of a medium are, to a large extent, limited to those effects linear and quadratic in the applied field. Of these, the linear electro-optic effect is observed only in media that lack a center of inversion. The quadratic effect, on the other hand, is universal in the sense that it occurs in all media, irrespective of symmetry. Generally, when the two occur together, the quadratic effect is much smaller, but nevertheless, in some instances in technological applications based on the linear effect, is viewed as a disturbance. However, there are configurations in noncentrosymmetric crystals for which symmetry requirements veto the exis-

tence of the linear effect; thus the quadratic response is the leading electro-optic one.

Since the initial realization by Billings² of the practical applications of electro-optics, crystals of the noncentrosymmetric KDP (KH_2PO_4) family have received particular attention, with the linear electro-optic coefficients of most members having now been measured.³ However, the quadratic coefficients of these crystals are still not well established. This paper considers the quadratic electro-optic effect exhibited by KDP and ADP ($\text{NH}_4\text{H}_2\text{PO}_4$) single crystals for those light paths and field directions for which the linear effect does not occur. Although considerable attention has been given to the quadratic electro-optic effect in these crystals in the past and numerous results have been published for its coefficients, there exists a large discrepancy in the reported data. Such data for both KDP and ADP have been tabulated⁴ and the discrepancy in results noted by a number of authors.^{5–12} As an example, values given by Perfilova and Sonin⁵ for KDP are (in units of $\text{m}^2 \text{ V}^{-2}$) $|g_{xxxx} - g_{yyxx}| = 2.6 \times 10^{-18}$ and $|n_o^3 g_{xxxx} - n_e^3 g_{zzxx}| = 13.5 \times 10^{-18}$; the corresponding ones for ADP are 1.7×10^{-18} and 16.5×10^{-18} . In contrast, other authors^{6,7} quote for KDP (in units of $\text{m}^2 \text{ V}^{-2}$), $|g_{xxxx} - g_{yyxx}| = 2.5 \times 10^{-20}$ and $|n_o^3 g_{xxxx} - n_e^3 g_{zzxx}| = 12 \times 10^{-20}$, and for ADP, $|g_{xxxx} - g_{yyxx}| = 4.7 \times 10^{-20}$. Closer inspection of the results published in the literature reveals that they may be divided into two separate sets that differ by a factor of ~ 100 .^{5–12} Of the values obtained by different

methods, those derived earlier by static means are of order of magnitude $10^{-18} \text{ m}^2 \text{ V}^{-2}$ and are larger than the equivalent dynamic values. The difference in these results cannot be explained in terms of either measurement error or a dependence of the coefficients on temperature, wavelength, or the frequency of the modulating field. All these results were recorded at room temperature, at a wavelength between 500 and 633 nm, and with an electric field of a frequency in the range dc to ~ 500 Hz. To explain the spread, it had been suggested previously that in certain cases the theoretical conditions forbidding the existence of the linear electro-optic effect were not precisely realized in practice; thus the measured response was due to both the linear and the quadratic effects, yielding misleading results for the latter.¹ Measurement techniques, specifically those employing static fields, which do not distinguish the linear and quadratic responses, may be regarded as suspect, and results so obtained should be treated with caution. Yet, despite this, it is largely the static results for KDP-type crystals that are quoted in the literature (see, for example, Landolt-Börnstein³ and Yariv and Yeh¹³). In this regard the remeasurement of the quadratic electro-optic coefficients in these crystals is important in order to establish reliable values and to lay to rest incorrect perceptions concerning their magnitude. As is apparent below, these measurements also throw light on the origin of the coefficients.

It is mentioned in passing that literature values of electrostrictive coefficients for KDP and ADP also exhibit a large spread.^{14–18} Some of these values were measured recently with the actively stabilized interferometer described in this paper. Although reported elsewhere,¹⁹ these results are repeated here for calculational purposes. (See Table 3.)

This paper describes an experimental investigation of the quadratic electro-optic coefficients of KDP and ADP crystals for configurations that theoretically preclude the existence of the linear electro-optic effect. The interferometric technique adopted offers the advantages of measuring individual coefficients of the electro-optic effect and, furthermore, of yielding the sign of the coefficients. In addition, the measurements lead to a deeper understanding of the nature of the nonlinear susceptibility that is responsible for the quadratic electro-optic effect in these crystals.

2. INVESTIGATION BY THE INTERFEROMETRIC METHOD

Shown in Fig. 1 is a schematic diagram of the Michelson interferometer and electronic equipment used in the measurement of the quadratic electro-optic and electrostrictive coefficients. The sensitivity of the intensity variation to small changes in optical path length is greatest at a point halfway between the positions of maximum and minimum intensities of the pattern.²⁰ With the system operated in this way the crystal under investigation was placed in the measurement arm of the interferometer, allowing propagation of the light beam from a 30-mW He-Ne laser along either its crystallographic y or z axis. When a low-frequency electric field was applied to the crystal, the light passing through it experienced an in-

duced change in optical path length Δd . This path-length variation may be related to the quadratic electro-optic effect through the change in the refractive index of the sample Δn and also to the material's electrostrictive strain, which alters its length by ΔL . Then

$$\Delta d = L\Delta n + (n - n_m)\Delta L, \quad (2)$$

where n is the field-free refractive index of the crystal for propagation along the wave front normal in the direction of the unit vector σ and for the particular polarization used, L is the field-free length of the crystal, Δn and ΔL are the corresponding field-induced changes in these quantities on account of the quadratic electro-optic and electrostrictive effects, respectively, and n_m is the refractive index of the medium surrounding the crystal.

The eigenvector theory of light propagation in a homogeneous anisotropic dielectric^{13,21} has been extended to describe the quadratic electro-optic effect for arbitrary directions of the light path and applied field. [See Eq. (8) in Ref. 1.] It follows from this theory that, for light propagating along the crystallographic y axis of a KDP-type crystal, to which a field is applied in the x direction, the field-induced changes in refractive index in Eq. (2) are

$$\Delta n_x = -\frac{1}{2}n_o^3 g_{xxxx} E_x^2, \quad (3)$$

$$\Delta n_z = -\frac{1}{2}n_e^3 (g_{zzxx} + n_o^2 r_{yzx}^2) E_x^2, \quad (4)$$

for the incident light polarized, respectively, parallel to the x and the z axes. The accompanying change in crystal length is

$$\Delta L_y = \gamma_{yyxx} L_y E_x^2. \quad (5)$$

For propagation along the optic axis and the incident light polarized at an angle α to the x axis, the corresponding results are

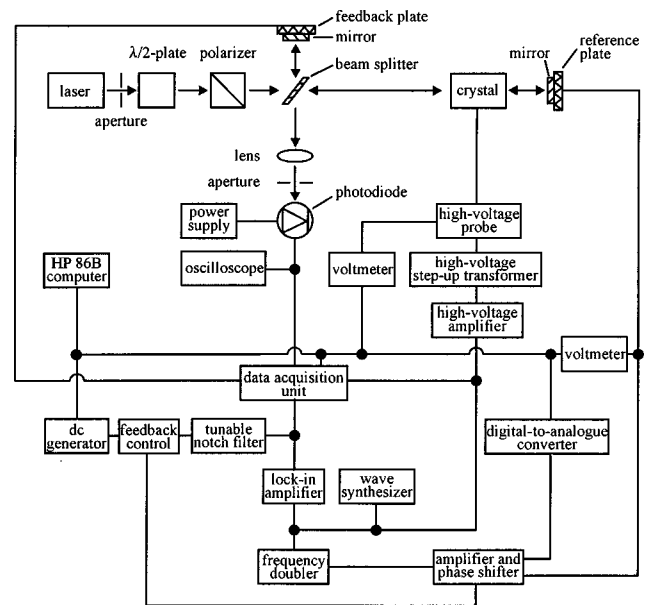


Fig. 1. Schematic diagram of the Michelson interferometer and the optical and electronic components used in the experiment.

$$\Delta n_z(\alpha) = -\frac{1}{2}n_o^3[g_{xxxx}\cos^2\alpha + (g_{yyxx} + n_e^2r_{yzx}^2)\sin^2\alpha]E_x^2, \quad (6)$$

$$\Delta L_z = \gamma_{zzxx}L_zE_x^2. \quad (7)$$

In Eqs. (3)–(7), n_o and n_e are the ordinary and the extraordinary refractive indices, respectively, E_x is the amplitude of the field applied to the crystal along the [100] direction, r_{yzx} is a linear electro-optic coefficient, and γ_{yyxx} and γ_{zzxx} are electrostrictive coefficients. Equation (6) is an approximation derivable only for propagation along the optic axis, for which the field-free refractive indices of each polarization eigenvector are identical, and their field perturbations are experimentally insignificant except in a difference such as Δn_z . Consequently, we do not express Eqs. (3) and (4) in a form analogous to Eq. (6).

The determination of the electrostrictive contribution in Eq. (2) that was made in this investigation involved placing the crystal in two media of distinctly different refractive indices.¹⁹ Those chosen were dry air with $n = 1.0003$ ²² and silicon oil, namely, T & C Chemicals DC 704 diffusion pump fluid, the refractive index of which at room temperature was found to be 1.5572.

An experimental consideration that required attention concerned the possibility of the two environments in which the samples were placed, displaying a quadratic effect themselves, in the form of the Kerr effect. As the quadratic effect is a property of all media, it could be that the fringing field around the edges of the specimen in the path of the propagating beam induced a significant birefringence quadratic in the field, especially in the oil. This would in turn influence the determination of the induced optical path-length changes. The molar Kerr constant for nitrogen, which would give a measure of the birefringence induced in air, has been measured and is $0.30 \times 10^{-27} \text{ C}^2 \text{ m}^5 \text{ J}^{-2}$ at 21 °C and 632.8 nm,²³ which is equivalent to $g = 3.4 \times 10^{-25} \text{ m}^2 \text{ V}^{-2}$. Compared with the field-induced changes in the refractive index of the crystal, the effect of the air is negligible. The g coefficient for silicon oil can be deduced from the literature,²⁴ namely, $1.6 \times 10^{-21} \text{ m}^2 \text{ V}^{-2}$ at room temperature and 632.8 nm. Calculations have shown that the response of the oil owing to the fringing electric field was less than 1% of that of the crystal in all configurations used.²⁴

The approach adopted in this experiment involved a compensation method. In this approach, which is similar in some respects to that used to determine the quadratic electro-optic effect in LiF^{25} and $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 3\text{H}_2\text{O}$,²⁶ the optical path-length variation induced in the crystal in the measurement arm of the interferometer was nulled by a second induced path-length change of known sign and magnitude. This reference effect was also produced in the measurement arm by attaching its mirror to a piezoceramic disk. A voltage applied across this disk led to a controlled translation of the mirror. The piezoelectric response of the reference ceramic was accurately calibrated at the frequency of the applied field and also over the same range of voltages used in the compensation procedure of the experiment. The change in the optical path length was established to be linear over the range of voltages used and to be free of any hysteresis. The calibra-

Table 1. Dimensions L_i , $i=x, y, z$ in Millimeters, along the i Crystallographic Axis of the Crystals Studied

| Crystal | L_x | L_y | L_z |
|---------------|-----------------|------------------|------------------|
| KDP | 4.99 ± 0.01 | 50.05 ± 0.02 | 49.77 ± 0.02 |
| ADP (larger) | 5.01 ± 0.02 | 50.27 ± 0.02 | 51.22 ± 0.02 |
| ADP (smaller) | 7.06 ± 0.02 | 34.58 ± 0.04 | 35.54 ± 0.02 |

tion procedure was based on determining the field-induced optical path-length difference from a measure of the resulting change in intensity of the interference pattern when balanced at its most sensitive point.

To allow compensation of the two induced path-length changes in the interferometer, the voltage applied to the ceramic was such that the variation in optical path length that it induced was at the same frequency as that due to the crystal but in antiphase to it. The computer-controlled apparatus employed in this study was actively stabilized against low-frequency environment noise to keep the interference pattern viewed by the photodiode at its most sensitive point for the duration of the experiment. This was achieved by controlling the length of the reference arm of the interferometer by a piezotransducer element to which the mirror in that arm was attached and by monitoring the voltage to the piezotransducer by means of a feedback circuit. This circuit monitored the dc and low-frequency (<20-Hz) components of the photodiode output signal, compared these to a reference dc voltage that was set to equal the dc photodiode output signal when the system was balanced at the most sensitive point, and then applied the phase-inverted difference of these signals to the piezotransducer element. This actively drove the interferometer back to the most sensitive point and in the process nulled any low-frequency noise. As a precautionary measure, a notch filter was placed before the feedback circuit to filter out the measurement signal, thus ensuring that the circuit did not view any portion of this signal and thus affect it in any way. By means of this computer-driven apparatus, with its modulation techniques in conjunction with a lock-in amplifier, electronic stabilization, and data-acquisition system, electric-field-induced path-length changes of the order of 1 nm were detectable in the crystals studied. Comparable or even greater sensitivity has been obtained by other researchers in a range of studies by employing electronic or optical controls in their interferometer, usually a Michelson or a Mach-Zehnder.^{27,28} However, these applications have not involved measurement of the quadratic electro-optic effect in a noncentrosymmetric crystal. Because of the large number of readings taken under computer control in this experiment, the need to maintain the interference pattern at its most sensitive point throughout each measurement run, by overcoming drift, was paramount. The active stabilization technique used ensured this and provided sufficient sensitivity for the effects being measured.

Three separate crystals, one KDP and two ADP, were investigated in this study, each cut in the form of a right parallelepiped. So prepared, the faces of each specimen were parallel to the xy , xz , and yz planes of the crystallo-

graphic axes. The dimensions of the crystals are shown in Table 1. To apply an electric field parallel to the x crystallographic axis, each sample was coated with conducting paint on its two faces parallel to the yz plane. The specimens were placed in the measurement arm of the interferometer and positioned so that the beam passed approximately halfway between the electrode plates. Measurements were then conducted for light propagation at several such points across the entrance face of each crystal. A high-voltage amplifier allowed a modulated field of frequency 391 Hz to be applied to each specimen, of variable amplitude up to $5 \times 10^5 \text{ V m}^{-1}$. In these investigations the crystal rested freely on its support, and since the frequency of the field was well below that of mechanical resonance of the crystal, it could be considered mechanically free.

3. RESULTS

From the compensation-voltage measurements for a particular configuration of crystal, field direction, light path, and polarization state, the appropriate combination of quadratic electro-optic and electrostrictive contributions could be determined. Some examples of the results obtained are plotted in Fig. 2. These two graphs apply, respectively, to KDP and ADP crystals when placed in a dry air environment, for z propagation, and with polarization of the incident light at various angles α to the crystallographic x axis. From the intercept and the slope of such

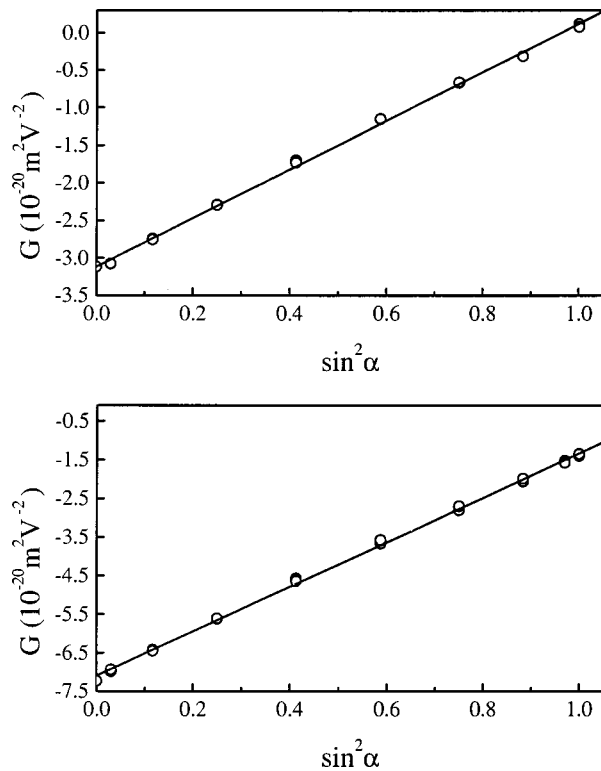


Fig. 2. Plots for z propagation of G as a function of $\sin^2 \alpha$, where from Eqs. (2), (6), and (7), $G = -2\Delta d/(n_o^3 L_z E_x^2) = (g_{yyxx} - g_{xxxx} + n_e^2 r_{yzx})\sin^2 \alpha + g_{xxxx} - 2(n_o - n_a)n_o^{-3}\gamma_{zzxx}$, and α is the angle between the plane of the incident polarized beam and the x crystallographic axis of the crystal. The upper plot is for KDP in air of refractive index n_a , the lower plot for ADP in air.

Table 2. Values of n_o , n_e , and r_{yzx} for KDP and ADP at 21 °C and 632.8 nm

| Crystal | n_o^* | n_e^* | r_{yzx}^{**} ($10^{-12} \text{ m V}^{-1}$) |
|---------|---------|---------|--|
| KDP | 1.5075 | 1.4670 | 8.8 |
| ADP | 1.5222 | 1.4773 | 23.4 |

*Values computed from data in Ref. 29.

**Values listed in Ref. 3.

Table 3. Quadratic Electro-Optic and Electrostrictive Coefficients of KDP and ADP at Room Temperature Measured in this Study in Units of $10^{-20} \text{ m}^2 \text{ V}^{-2}$

| Coefficient | KDP | ADP |
|----------------------|----------------|----------------|
| g_{xxxx}^* | -3.4 ± 0.5 | -7.4 ± 1.0 |
| g_{yyxx} | -0.2 ± 0.4 | -1.7 ± 0.9 |
| g_{zzxx} | -0.7 ± 0.4 | -1.4 ± 0.9 |
| γ_{yyxx}^{**} | 1.5 ± 1.4 | -2.3 ± 3.0 |
| γ_{zzxx}^{**} | -1.0 ± 1.3 | -0.7 ± 3.1 |

*For the KDP crystal and the smaller of the two ADP crystals two independent values of g_{xxxx} were measured, namely, in units of $10^{-20} \text{ m}^2 \text{ V}^{-2}$, -3.43 and -3.44 for KDP and -7.47 and -7.40 for ADP.

**Values quoted in Ref. 19.

graphs for the crystal in air and oil, values were obtained for the quantities $g_{xxxx} - 2(n_o - n_m)n_o^{-3}\gamma_{zzxx}$ and $g_{yyxx} - 2(n_o - n_m)n_o^{-3}\gamma_{yyxx} + n_e^2 r_{yzx}^2$. Results were also obtained for $g_{xxxx} - 2(n_o - n_m)n_o^{-3}\gamma_{yyxx}$ and $g_{zzxx} - 2(n_e - n_m)n_e^{-3}\gamma_{yyxx} + n_o^2 r_{yzx}^2$, corresponding to light propagating along the y axis and polarized parallel and perpendicular to the field, respectively. The values of n_o , n_e , and r_{yzx} for KDP and ADP that are used in the above four expressions are listed in Table 2. Use of the values of r_{yzx} for KDP and ADP shows that their contributions are both approximately equal to $1.5 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$. From suitable combinations of these results the sign and the magnitude of each coefficient of interest could be calculated. Those for the electrostrictive contribution in Eq. (2) were found, as reported previously,¹⁹ from measurements performed for identical experimental conditions except for the medium in which the crystal was immersed. This technique allowed Δn and ΔL in Eq. (2) to be determined separately from the different observed Δd values for the air and the silicon oil that were used. (See Ref. 19 for a more detailed account.) With these electrostrictive values known, those of g_{xxxx} , g_{yyxx} , and g_{zzxx} were then calculated. In the case of g_{xxxx} there was some degeneracy, and the final result quoted is the average of the two calculated for each crystal. All these results are summarized in Table 3.

4. DISCUSSION OF EXPERIMENTAL RESULTS

The results in Table 3 for the sign and the magnitude of the individual electro-optic coefficients g_{xxxx} , g_{yyxx} , and g_{zzxx} are, to our knowledge, the first of their kind for these crystals. An earlier interferometric experiment by some of the present authors yielded values for KDP at room temperature for three of the four combinations of coeffi-

cients in Section 3.⁷ However, as these were measured with the crystal in an oil environment only, it was not possible to evaluate separately the electro-optic and the electrostrictive coefficients. In addition, the calibration of the reference piezoceramic in the earlier experiment is questionable, in that a static field was used, ~ 100 times stronger than the ac fields in the nulling measurements.⁷ Apart from a possible frequency effect, the response of the piezoceramic was since found to be nonlinear over such a large voltage range. By contrast, the calibration in the present investigation was performed at the same frequency and over the same range of voltages as those in the experiment, and the displacement of the mirror attached to the piezoceramic was found to be linear over this range.

The results obtained for KDP in the present experiment for $g_{xxxx} - g_{yyxx}$ of $-(3.2 \pm 0.2) \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$ and for $n_o^3 g_{xxxx} - n_e^3 g_{zzxx}$ of $-(9.5 \pm 2.0) \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$ are in good agreement with that of $|3.4 \pm 0.1| \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$ and $|9.3 \pm 0.6| \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$, respectively, measured recently by dynamic polarimetric means.⁴ Similarly for ADP, our values for $g_{xxxx} - g_{yyxx}$ of $-(5.7 \pm 0.5) \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$ and for $n_o^3 g_{xxxx} - n_e^3 g_{zzxx}$ of $-(21.4 \pm 4.6) \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$ compare favorably with those of $|6.0 \pm 0.5| \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$ and $|20.4 \pm 0.6| \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$, respectively, obtained in a recent dynamic polarimetric investigation.^{4,11}

It may be noted from Table 3 that certain errors are relatively large, especially in g_{yyxx} for KDP and in all the γ coefficients. The reason is that all the coefficients in Table 3 are obtained from the difference of terms (see Section 3), and the errors in these terms are additive. For the particular coefficients above the difference is relatively small.

5. NATURE OF THE QUADRATIC ELECTRO-OPTIC EFFECT IN KDP-TYPE CRYSTALS

To study the nature of the nonlinearities that are responsible for the quadratic electro-optic effect, it is first necessary to distinguish the different contributions to the change in the impermeability tensor ΔB_{ij} that is induced by the applied low-frequency field. For a crystal that is free, as opposed to clamped, this change may be expressed in terms of the notation in Refs. 30 and 31, namely,

$$\Delta B_{ij} = g_{ijkl} E_k E_l = (\bar{g}_{ijkl} + p_{ijmn} \gamma_{mnkl}) E_k E_l + q_{ijkl} \sigma_{kl}. \quad (8)$$

In this, \bar{g}_{ijkl} is the true (or so-called primary) quadratic electro-optic coefficient, whereas p_{ijkl} and q_{ijkl} are the elasto-optic and piezo-optic coefficients, respectively, and σ_{ij} is the stress from the electrostatic attraction between the electrodes.

The primary quadratic electro-optic effect is known to originate from two sources.³² In one of these the lattice ions are displaced by the applied field, thereby changing the electronic susceptibility, whereas the other arises from the displacement of electrons within an ion. Accordingly one may write

$$\bar{g}_{ijkl} = \bar{g}_{ijkl}^{\text{ion}} + \bar{g}_{ijkl}^{\text{elec}}. \quad (9)$$

Because of their distinct physical origins, the lattice and the electronic coefficients in Eq. (9) are related to different effects: for instance, $\bar{g}_{ijkl}^{\text{ion}}$ is related to the second-order strain derivative of the electronic susceptibility,³² and $\bar{g}_{ijkl}^{\text{elec}}$ is related to the third-order optical susceptibility $\chi_{ijkl}^{(3)}$ that accounts for four-wave mixing and the nonlinear refractive index.¹³ In addition, it has been found in alkali halides that $\bar{g}_{ijkl}^{\text{elec}}$ contributes to electric-field-induced first-order Raman scattering³³ and to hyper-Raman scattering.³⁴ Yet, by contrast, it can be shown, by use of the classic approach in Ref. 32 or that in Ref. 33, that both the lattice and the electronic contributions have to be taken into account for second-order Raman scattering.

From the theory in Refs. 30 and 31 the stress that is due to the electrostatic force on our crystal samples, which were coated with conducting paint on their faces parallel to the yz plane, is $\sigma_{xx} = (1/2)\epsilon_0 \epsilon_{xx} E_x^2$. Using published values³ of the piezo-optic coefficient, namely, in units of $10^{-12} \text{ m}^2 \text{ N}^{-1}$, for KDP, $q_{xxxx} = 4.15$, $q_{xxyy} = 4.08$, $q_{xxzz} = 1.12$, and $q_{zzzz} = 0.44$, and for ADP, $q_{xxxx} = 4.40$, $q_{xxyy} = 3.71$, $q_{xxzz} = 0.34$, and $q_{zzzz} = 2.65$, one finds that the contribution of the electrostatic force, given by the last term in Eq. (8), to the coefficients g_{xxxx} , g_{yyxx} , and g_{zzxx} in Eq. (1) is, in units of $10^{-22} \text{ m}^2 \text{ V}^{-2}$, for KDP, 7.9, 7.8, and 6.9, and for ADP, 11, 9.2, and 5.0, respectively.

Much more significant, especially for KDP, is the elasto-optic-electrostrictive contribution in Eq. (8) to the above g -tensor components, which is found to be, now in units of $10^{-20} \text{ m}^2 \text{ V}^{-2}$, for KDP, 1.2, 1.1, and 1.0, and for ADP, -0.02 , -0.21 , and -0.12 , respectively. In this calculation the elasto-optic coefficients used were taken from tables,³ namely, for KDP, $p_{xxxx} = 0.287$, $p_{xxyy} = 0.282$, $p_{xxzz} = 0.174$, $p_{zzxx} = 0.241$, and $p_{zzzz} = 0.122$, and for ADP, $p_{xxxx} = 0.319$, $p_{xxyy} = 0.277$, $p_{xxzz} = 0.169$, $p_{zzxx} = 0.197$, and $p_{zzzz} = 0.167$. The electrostrictive coefficients are those reported in Ref. 19 (see Table 3), together with $\gamma_{xxxx} = 2.0$, estimated roughly for KDP from the temperature dependence of the electrostrictive coefficients measured by Sysoev,¹⁶ and $\gamma_{xxxx} = 2.3$, both in units of $10^{-20} \text{ m}^2 \text{ V}^{-2}$, obtained for ADP from dynamic measurements.¹⁵

Using in Eq. (8) the above results for the piezo-optic, the elasto-optic, and the electrostrictive coefficients, we calculated values of the true quadratic electro-optic coefficients from our measurements. In units of $10^{-20} \text{ m}^2 \text{ V}^{-2}$ they are for KDP, $\bar{g}_{xxxx} = -4.7$, $\bar{g}_{yyxx} = -1.4$, and $\bar{g}_{zzxx} = -1.8$, and for ADP, $\bar{g}_{xxxx} = -7.5$, $\bar{g}_{yyxx} = -1.6$, and $\bar{g}_{zzxx} = -1.3$. The nature of the true quadratic electro-optic coefficient is here investigated in terms of the C_{ijkl} coefficient, defined by

$$C_{ijkl} = \bar{g}_{ijkl}^{\text{ion}} / \bar{g}_{ijkl}^{\text{elec}}. \quad (10)$$

Because the analogous ratio for the linear electro-optic effect is usually called the Faust–Henry coefficient,³⁵ that in Eq. (10) is here termed the quadratic Faust–Henry coefficient.

The relation between $\bar{g}_{ijkl}^{\text{elec}}$ and $\chi_{ijkl}^{(3)}$ that was referred to earlier in this section is¹³

$$\bar{g}_{ijkl}^{\text{elec}} = -12 \epsilon_{ii}^{-1} \epsilon_{jj}^{-1} \chi_{ijkl}^{(3)}, \quad (11)$$

where ϵ_{ii} is a principal component of the optical-frequency permittivity tensor. Only two components of $\chi_{ijkl}^{(3)}$ appear to have been measured for KDP and ADP. From the data in Ref. 3 one obtains, in units of $10^{-22} \text{ m}^2 \text{ V}^{-2}$, $\chi_{xxxx}^{(3)} = 0.63$ and $\chi_{yyxx}^{(3)} = 0.063$ for KDP and $\chi_{xxxx}^{(3)} = 1.2$ and $\chi_{yyxx}^{(3)} = 0.33$ for ADP. Using these and describing their dispersion in terms of the Miller δ coefficient, the use of which to predict the magnitude of the third-order optical susceptibility is discussed in Ref. 36, we obtain from Eq. (11) the values, in units of $10^{-22} \text{ m}^2 \text{ V}^{-2}$, for KDP, $\bar{g}_{xxxx}^{\text{elec}} = -1.5$ and $\bar{g}_{yyxx}^{\text{elec}} = -0.2$, and for ADP, $\bar{g}_{xxxx}^{\text{elec}} = -2.7$ and $\bar{g}_{yyxx}^{\text{elec}} = -0.7$.

From these and our measurements the corresponding quadratic Faust–Henry coefficients are for KDP, $C_{xxxx} \sim 300$ and $C_{yyxx} \sim 1000$ and for ADP, $C_{xxxx} \sim 300$ and $C_{yyxx} \sim 200$.

If use is made of a different calibration standard for $\chi_{ijkl}^{(3)}$ (for example, that in Ref. 37) from that in Ref. 3, or if the δ coefficient is only approximately constant over the frequency range considered, these quadratic Faust–Henry coefficients would change somewhat but, nevertheless, would still imply a predominantly ionic nature of the true quadratic electro-optic coefficients of KDP and ADP.

The above values of C_{xxxx} and C_{yyxx} for KDP may be compared with its Faust–Henry coefficient for the linear electro-optic effect, calculated as follows. According to Ref. 3, the values of the linear electro-optic coefficient r_{yzx} of KDP at constant strain and constant stress are practically equal. From the value of r_{yzx} in Table 2 and $d_{36} = 0.39 \times 10^{-12} \text{ m V}^{-1}$ for its second-harmonic susceptibility, calibrated in Ref. 38 at $\lambda = 1.064 \mu\text{m}$ by means of the absolute standard proposed in that study, and using the Kleinman conjecture for the second-harmonic generation coefficient, we obtain $C_{yzx} \sim 30$. Comparing this with the quadratic values above shows that for KDP at room temperature the electronic contribution to the true quadratic electro-optic effect at low frequency is even smaller than it is for the linear effect. By contrast the Faust–Henry coefficient for the linear effect in gallium phosphide is -0.5 ,³⁵ so that here the lattice and electronic contributions are comparable. This is not the case for KDP for either its linear or quadratic effects.

6. CONCLUSION

The values of the quadratic electro-optic coefficients measured in this study by use of a dynamic field and an actively stabilized interferometer are two orders of magnitude smaller than some published results obtained with a static field. (See, for example, Ref. 5.) Although undertaken in a different context, a recent computer analysis of the accuracy of measurement in the two experimental techniques shows that the use of a static field may lead to considerably higher results.³⁹ The good agreement between the values reported here and those measured by means of a dynamic polarimetric method⁴ also gives confidence in the present values.

An interpretation of our results on the basis of the quadratic Faust–Henry coefficients for KDP and ADP shows that the nonlinearities responsible for the quadratic electro-optic effect in these crystals at room temperature,

and presumably in other members of this family, are due to the nonlinear interaction of the applied electric field with the crystal lattice. The purely electronic contribution may be neglected.

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