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Absolute Signs of Second-Harmonic Generation Coefficients of Piezoelectric Crystals

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This paper describes the measurement of the absolute signs of the nonlinear optical coefficients d_{ij} that give rise to second-harmonic generation in piezoelectric crystals. The measurements were made with a repetitively Q-switched Nd-yttrium aluminum garnet (Nd-YAG) laser (1.064 μ) and involve relative sign determinations between two crystals followed by a comparison of at least one of them with d_{14} of GaP, which has been shown previously to be positive with respect to the +[111]. To determine the unique directions in the crystals studied, several different methods were used, including: the piezoelectric effect, the pyroelectric effect, the etching behavior, and the electric field aligned spontaneous polarization. The crystals investigated included the following: zinc-blende crystals (ZnSe, ZnTe, and CdTe), wurtzite crystals (ZnO, BeO, CdS, and CdSe), ferroelectric crystals [LiTaO₃, LiNbO₃, BaTiO₃, Ba₂NaNb₅O₁₅, Gd₂(MoO₄)₃, and Tb₂(MoO₄)₃], and several other crystals (LiIO₃, LiGaO₂, LiCHO₂·H₂O, and quartz). Strong absorption of the second harmonic complicates the interpretation of the experimental results for ZnTe, CdTe, and CdSe. The present results and those of several recent theoretical predictions are in good agreement.

I. INTRODUCTION

Recently, there have been a number of useful calculations of the signs and/or the magnitudes of the nonlinear optical coefficients d_{ij} that describe second-harmonic generation (SHG) and optical parametric interactions in piezoelectric crystals. One of the more important earlier predictions,[1,2] which was for crystals with wurtzite (w) and zinc-blende (z) structures, was that

$$d_{33}(w) = -2d_{31}(w) = (2/\sqrt{3})d_{14}(z).$$

Of the several papers that have considered SHG with III-V compounds,[2-5] the most successful utilized the electrodynamical bond-charge model,[2] which led to predictions of signs and magnitudes in good agreement with experiment. In the case of the II-VI compounds, the bond-charge model, modified to take into account unequal atomic radii,[6] was even able to account for the observed[7] sign reversal of the d's in going from CdS to ZnO. Other publications have included predictions for several of the niobates,[8] HIO₃ and LiIO₃,[9] quartz,[6] and the general class of polar crystals.[10]

The early work having to do with sign predictions, notably that of Levine,[2] and Jeggo and Boyd,[8] stimulated the present rather extensive experimental investigation aimed at determining the absolute signs of the d's for a variety of different crystals. Prior to the present measurements, the only published determinations of the absolute signs of d's were for several crystals with the zinc-blende structure, namely, GaP,[11] and GaAs, InAs, and GaSb.[12] Some of the present results have been described previously in abbreviated letter form[7]; however, this paper presents a detailed description of the experimental measurements and many heretofore unpublished results.

The magnitudes of the d's were not, in general, determined during the course of this study since they had been measured previously for most of the crystals investigated, and the results are included in an excellent recent summary of experimental data.[13]

II. DETERMINATION OF UNIQUE CRYSTALLINE DIRECTIONS

The absolute signs of d only have meaning when they are related to an absolute direction in the piezoelectric

crystal. In general, these directions can be determined by x-ray analyses,[14] etching,[15] or piezoelectric tests.[16] For crystals belonging to polar crystal classes (crystals with a spontaneous polarization), one can also use the pyroelectric effect,[17] and for ferroelectric crystals (reversible pyroelectrics) the direction of the spontaneous polarization P_s. Of the above-mentioned techniques, only the x-ray method allows one to relate to the absolute crystal structure, that is, to the arrangement of atoms in the crystal. The theoretical predictions of the absolute signs of d are of course relative to the absolute crystal structure.

For the III–V and II–VI crystals, the outward normal from the metal A face (element II or III face) is defined as $+[111]$ and $+z$ for the zinc-blende and wurtzite forms, respectively. With most of the III–V and II–VI crystals investigated, the A faces were identified via etching procedures and/or piezoelectric measurements which had been previously related to the absolute crystal structures through x-ray analyses.[15]

For the general class of polar crystals, the $+z$ direction is taken as the outward normal from the z-cut face that develops a negative charge on compression along z.[16] This definition is consistent with that given above for the wurtzite crystals (polar) which were studied. For the ferroelectric crystals investigated, $+z$ is also the direction of $\vec{P}_s$. In addition, these definitions for polar crystals are consistent with $+z$ defined as the outward normal from the z-cut face that develops a positive charge on cooling the crystal when dP_s/dT is negative (usually the case[18]), and a negative charge on cooling when dP_s/dT is positive.

The actual methods used to determine the unique directions of the crystals investigated belonging to the classes mentioned above, and other classes as well, are given in Table I. In many cases several different techniques were employed for a given crystal.

The first determination of an absolute sign for a d_{ij} was by Nelson and Turner,[11] who made use of the Faust-Henry experiment[19] to show that d_{14} is positive for GaP with respect to the $+[111]$ as defined above. Subsequently, Wynne and Bloembergen[12] used an interference technique to compare GaAs, InAs, and GaSb with GaP and also found their d_{14}'s to be positive. These signs are in agreement with Refs. 2, 4, and 6, but in disagreement with Ref. 3.

III. EXPERIMENTAL TECHNIQUE

The measurement involves relative sign determinations between two crystals for one or more of their d's followed by a comparison of at least one of them with GaP and/or GaAs, both of which are reported to have a positive d_{14}. The technique used is in effect a modification of experimental methods developed earlier by Bloembergen and collaborators.[12,20]

TABLE I. Determination of unique directions.

Material	Piezo-electric test	Pyro-electric test	Etch test	Spontaneous polarization
GaP(z)	a, b		c, d	
GaAs(z)	a, e		d, f	
ZnTe(z)			g, h, i	
CdTe(z)			g	
ZnSe(z)	j, k			
ZnO(w)	l, e	m, n	n	
CdS(w)	l, e		g	
BeO(w)	l, o	m, o	o	
CdSe(w)			g, p	
LiTaO₃	q, r	s		t
LiNbO₃	q, r	s		t
Ba₂NaNb₅O₁₅	q, r	s		
Gd₂(MoO₄)₃	q, r	s		
Tb₂(MoO₄)₃	q, r	s		
BaTiO₃				t
LiIO₃	q, r			
LiGaO₂	q, r	s		
LiCHO₂·H₂O	q, r			
Quartz(l)	u, r			

ᵃ A negative charge develops on the metal face on extension along $+[111]$.

ᵇ See Ref. 11.

ᶜ 10% Cl₂ in CH₃OH.

ᵈ C. S. Fuller and H. W. Allison, J. Electrochem. Soc. **109**, 880 (1962).

ᵉ See Ref. 33 and references contained therein.

ᶠ 10% Br₂ in CH₃OH.

ᵍ E. P. Warekois, M. C. Lavine, A. N. Mariano, and A. G. Gatos, J. Appl. Phys. **33**, 690 (1962); **37**, 2203(E) (1966).

ʰ L. R. Shiozawa, J. M. Jost, and G. A. Sullivan, Aerospace Research Laboratories Technical Report No. ARL 68-0153, 1968 (unpublished).

ⁱ Concentrated HCl for 2 min. The Zn face becomes shiny and the Te face becomes dull. L. R. Shiozawa (private communication).

ʲ A positive charge develops on the metal face on extension along $+[111]$.

ᵏ The piezoelectric coefficient is assumed to have a positive sign as other II-VI compounds; see Ref. 33.

ˡ A positive charge develops on the metal face on extension along $+[001]$.

ᵐ A positive charge develops on the metal face on cooling.

ⁿ R. L. Barns, E. T. Keve, and S. C. Abrahams, J. Appl. Cryst. **3**, 27 (1970).

ᵒ S. B. Austerman, D. A. Berlincourt, and H. H. A. Krueger, J. Appl. Phys. **34**, 339 (1963).

ᵖ Concentrated HCl for 2 min. The Cd surface becomes shiny and the Se surface dull. L. R. Shiozawa (private communication).

�q A positive charge develops on extension along the polar axis on the face from which the outward normal is taken as positive.

ʳ See Ref. 16.

ˢ A positive charge develops on the (001) face, on cooling, from which the outward normal is the positive [001]; dP_s/dT is negative.

ᵗ An electric field was used to align the spontaneous polarization.

ᵘ For left-handed quartz, a positive charge develops on extension along the x axis on the face from which the outward normal is the positive x direction.

The second-order nonlinear polarization is defined by

$$P^{NL} = d(\mathcal{E}_1')^2, \qquad (1)$$

where $E_1' = \mathcal{E}_1' \exp i(k_1 x - \omega t)$ represents the fundamental wave propagating in the x direction in the
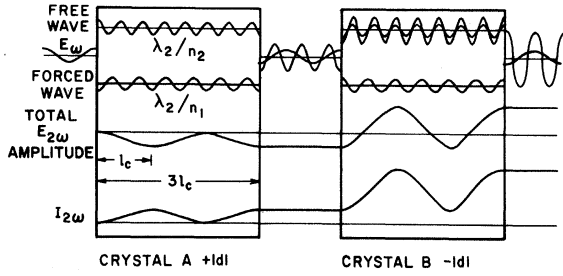
FIG. 1. Schematic drawing of SHG due to two identical crystals in series with their unique directions antiparallel. Reflections have been ignored and it is assumed that there is no dispersion between the two crystals. Each crystal contains three coherence lengths (l_c) and therefore exhibits a Maker SHG maximum. The fundamental wave E_ω enters crystal A from the left and generates free and forced second-harmonic waves which initially differ in phase by $\pm\pi$ as shown. The free waves from both crystals add in crystal B giving rise to constructive interference. The figure also shows the variation of the second-harmonic amplitude ($E_{2\omega}$) and intensity ($I_{2\omega}$) as the waves propagate through the crystals. If the two unique directions are parallel (not shown), destructive interference occurs in crystal B and no second-harmonic emerges from the pair of crystals.

piezoelectric medium with a refractive index n_1 at frequency ω and a propagation constant $k_1=\omega n_1/c=2\pi n_1/\lambda$. It is convenient to express d by

$$d=d^0\exp(i\varphi),\qquad(2)$$

with respect to the positive directions defined earlier where d^0 is real and positive. A negative d will therefore have $\varphi=\pm\pi$. The d's are expected to be real for lossless media,[12] which are discussed first. For the present purpose, the tensor nature of the nonlinear interaction can be ignored.

A. Transparent Crystals

Consider SHG in the first of two transparent crystals mounted in series. It can be shown that for plane waves, the second-harmonic field in vacuum at the end of a crystal platelet of thickness x_0 can be represented by[21,22]

$$E_2=-4\pi d\mathcal{E}_1^2/(n_2-n_1)(n_1+1)^2(n_2+1)$$
$$\times\{\exp[2i(k_1x_0-\omega t)]-\beta\exp[i(k_2x_0-2\omega t)]\},\quad(3)$$

with

$$\beta=2n_2(n_1+1)/(n_2+1)(n_2+n_1)\approx1,\qquad(4)$$

where n_2 is the refractive index of the nonlinear medium at frequency 2ω, $\mathcal{E}_1$ the fundamental field amplitude incident on the crystal, and $k_2=2\omega n_2/c=4\pi n_2/\lambda$. If the crystal is fabricated into a flat and parallel platelet suitable for the observation of Maker SHG fringes[23] and the path length $l\geq x_0$ in the crystal is adjusted such that $|E_2|$ is a maximum near normal incidence, i.e., $\Delta kl=(k_2-2k_1)l=N_{odd}\pi$, where N_{odd} is an odd integer,

Eq. (3) becomes

$$E_2=-\frac{4\pi d\mathcal{E}_1^2\exp[2i(k_1l-\omega t)]}{(n_2-n_1)(n_1+1)^2(n_2+1)}[1+\beta].\qquad(5)$$

Under these conditions it can be seen that the phase angle between the harmonic "forced wave"[21] [the inhomogeneous solution[22] or first term of Eq. (3)] and the fundamental squared at the front surface of the crystal, namely, $\varphi\pm\pi$ for $n_2>n_1$, is equal to the phase angle between the second-harmonic wave and the fundamental squared at the exit of the crystal except for a multiple of 2π. If $n_2<n_1$, i.e., the coherence length $l_c=\pi/\Delta k=\lambda/4(n_2-n_1)$ is negative, and the relative phase angle becomes φ.

If a second nonlinear crystal (B) is now positioned in the path of the fundamental and harmonic beams coming from the first crystal (A), interference effects can be observed which enable one to determine the relative phases and hence the relative signs of the two d's being compared. Assume $n_2>n_1$ for both crystals and that the medium between the two crystals is not dispersive. Then, the phase angle between the second-harmonic wave from crystal A and the fundamental squared at the front surface of crystal B, in general, defined by $\varphi_A'\pm\pi$, is in this case equal to $\varphi_A\pm\pi$. The second-harmonic wave from crystal A contributes to the "free wave"[21] [homogeneous solution[22] or second term in Eq. (3)] in crystal B. Since the phase angle between the free wave generated in crystal B and the fundamental squared just within the second crystal is φ_B, the phase difference between the two components of the free wave in crystal B will be $\varphi_A-\varphi_B\pm\pi$. Thus for $\varphi_A-\varphi_B=\pm\pi$, one has constructive interference and for $\varphi_A-\varphi_B=0$, destructive interference. This is evident in the expression below which describes the second-harmonic field within crystal B:

$$E_2'(B)\propto\{\exp[2i(k_1x-\omega t)]+[(n_1+1)/(n_2+1)]$$
$$\times(\gamma\exp[i(\varphi_A-\varphi_B)]-1)\exp[i(k_2x-2\omega t)]\}.\quad(6)$$

In Eq. (6), all quantities refer to crystal B except φ_A and γ, which is the ratio of the second-harmonic field amplitude in crystal B due to crystal A to that of the free wave due to crystal B alone. With crystal B also in the form of a flat and parallel platelet, and set (in the absence of crystal A) at a Maker-fringe maximum near normal incidence, the second-harmonic power P_2 emergent from the two crystals in series can be approximated by

$$P_2\propto\{4+\gamma[\gamma-4\cos(\varphi_A-\varphi_B)]\},\qquad(7)$$

where it has been assumed that for crystal B,

$$\beta=2n_2(n_1+1)/(n_1+n_2)(n_2+1)=1.$$

Figure 1 illustrates the two-crystal situation described above for the case where both crystals are set at

Maker SHG maxima and the crystals identical except that their unique directions are antiparallel so that $\varphi_A - \varphi_B = \pm\pi$. Reflections have been ignored. For the corresponding case (not shown in Fig. 1) with $\varphi_A = \varphi_B$, the two free waves would interfere destructively in crystal B with the result that no second-harmonic light would emerge from the pair of crystals.

As a result of uncertainties in γ due to beam divergence and other factors, it is usually not possible to deduce $\varphi_A - \varphi_B$ from Eq. (7) alone. To circumvent this difficulty, dispersion is introduced between the two crystals. Initially, the phase difference between the second-harmonic wave and the fundamental squared is adjusted to change by exactly 4π over the distance s between the two crystals, i.e., $\varphi_A' \pm \pi - (\varphi_A \pm \pi) = 4\pi$. By means of two identical crystals and Eq. (7), where now φ_A should be replaced by φ_A', it was found that when the enclosure housing the crystals, photomultiplier, etc., was nominally filled with dry CO_2, a distance s equal to 13.3 cm provided the desired 4π phase difference. This value for s is in agreement with estimates from published refractive index data on CO_2.[24] The CO_2 is then replaced slowly with He, which has a much smaller dispersion than CO_2,[24] thereby changing φ_A' by more than 2π so that over one cycle of Eq. (7) is scanned. Figure 2 shows typical data for d_{33} for two identical $LiNbO_3$ crystals mounted with their z axes parallel, i.e., $\varphi_A = \varphi_B$. As expected from Eq. (7), one observes a minimum in P_2 with a CO_2 atmosphere, which then goes through a maximum as the CO_2 is partially replaced by He. Thus, it is clear that when $P_2(CO_2)$ is a minimum, $\varphi_A = \varphi_B$ and the d's have the same signs. Likewise the two d's have opposite signs if $P_2(CO_2)$ is a maximum, i.e., $\varphi_A - \varphi_B = \pm\pi$.
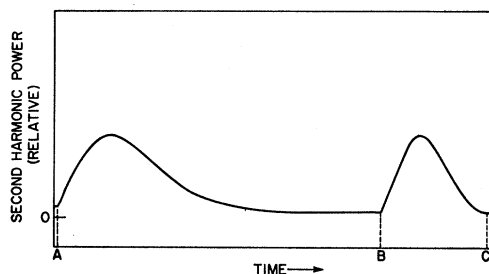
For these experiments the fundamental frequency was

FIG. 2. Second-harmonic power P_2 due to d_{33} emergent from two identical $LiNbO_3$ platelets mounted in series with their $+z$ directions parallel. Each crystal is separately adjusted to a Maker fringe maximum near normal incidence to the Nd–YAG laser beam. The atmosphere between the two crystals is slowly changed from air to essentially pure CO_2 by introducing CO_2 at a constant flow rate beginning at time A. A steady state is reached at time B, at which point the CO_2 flow is stopped and He is introduced at a constant rate. P_2 traces out a complete cycle between B and C. Since the values of P_2 at times B and C are both minima with the same value, the two d_{33}'s have the same phase shift, as expected.

TABLE II. Absolute signs and phases of SHG coefficients.

Transparent crystals						
	d_{14}	d_{33}	d_{31}	d_{32}	d_{22}	d_{11}
ZnSe(z)	+					
ZnO(w)		−	+			
BeO(w)[a]		−	−			
CdS(w)[b]		+	−			
LiTaO₃		−	−		+	
LiNbO₃[c]		−	−		+	
BaTiO₃		−	−			
Ba₂NaNb₅O₁₅[b]		−	−	−		
Gd₂(MoO₄)₃		−	−	+		
Tb₂(MoO₄)₃		−	−	+		
LiIO₃[d]		−	−			
LiGaO₂		−	−	+		
LiCHO₂·H₂O	+	e	−			
Quartz(l)						+

Absorbing crystals		
	$(\varphi_{14})_{\text{expt}}$	
	$(\varphi_{33})_{\text{expt}}$	$(\varphi_{31})_{\text{expt}}$
ZnTe(z)	0°	
CdTe(z)	±π	
CdSe(w)	$\pi - 44° \pm \pi$	$-49° \pm \pi$

[a] See Ref. 37 for the relative signs.

[b] See Ref. 10 for the relative signs.

[c] The relative signs of d_{22} and d_{31} were determined by J. E. Bjorkholm, Appl. Phys. Letters **13**, 36 (1968).

[d] Relative signs determined by J. Jerphagnon, Appl. Phys. Letters **16**, 298 (1970).

[e] SHG due to d_{31} could not be observed with the sample orientation used.

provided by a Nd–yttrium aluminum garnet (Nd-YAG) laser (1.064 μ) acoustically Q-switched at a 1-kHz rate. The unapertured multimode output beam was several mm in diam and had a peak power of about 400 W. For samples with a small cross section, an adjustable iris was utilized to limit the beam diameter to as small as about 1 mm. When comparing two crystals, the beam was never focused. However, for the determination of the relative signs of coefficients for a given crystal,[25] moderately focused beams were sometimes used.

The samples were fabricated into optically flat platelets, typically several mm thick, with the opposite sides parallel to about one minute of arc or less. In the case of ferroelectric crystals, only single domain regions were investigated.[26] The two crystals to be compared were mounted in series, each on a rotatable head with the unique direction known. State of the art detection methods were used.

B. Absorbing Crystals

The appropriate equations for absorbing crystals are obtained from Eq. (3) by allowing the refractive indices and hence k_1 and k_2 to be complex quantities, in par-
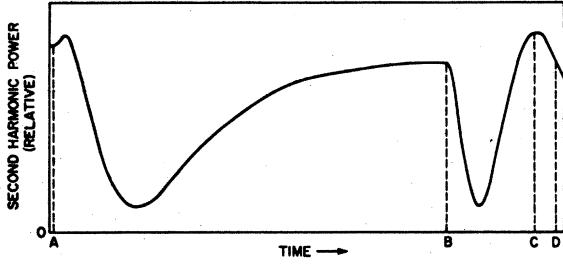
FIG. 3. Second-harmonic power P_2 due to d_{33} from CdSe and ZnO platelets using the same controlled dispersion technique described in the caption for Fig. 2. P_2 traces a complete cycle between times B and D. Since P_2 at point B does not correspond to an extremum of the He cycle between B and D, the relative phase of the two d_{33}'s is not simply 0 or $\pm\pi$. Analysis of these data shows that the relative phase between the two d_{33}'s is $\pi-44°\pm\pi$.

ticular

$$k_j = k_j' + \tfrac{1}{2}i\alpha_j, \qquad n_j = n_j' + i\lambda\alpha_j/4\pi j. \qquad (8)$$

The α_j are the power absorption coefficients. In the most general case, Eq. (3) becomes

$$E_2 = -\frac{8\pi\omega\mathcal{E}_1^2\, d\, \exp[2i(k_1'x_0 - \omega t) - \alpha_1 x_0]}{c(\Delta k' + i\alpha)(n_1+1)^2(n_2+1)}$$
$$\times \{1 - \beta\, \exp[i(\Delta k' + i\alpha)x_0]\}. \qquad (9)$$

In Eq. (9), $\alpha = \tfrac{1}{2}\alpha_2 - \alpha_1$ and β, defined earlier by Eq. (4), will also be complex via Eqs. (8).

Next consider two specific cases; first, SHG in GaP with a 1.06-μ laser. The present data show that $\alpha_1 \approx 0$, $\alpha_2 \approx 120$ cm^{-1}, and $\Delta k' \approx 5 \times 10^4$ cm^{-1}. For this case, Eq. (9) can be approximated by

$$E_2 = -\frac{4\pi\mathcal{E}_1^2\, d\, \exp[2i(k_1x_0 - \omega t)]}{(n_2' - n_1)(n_1+1)^2(n_2'+1)}$$
$$\times \{1 - \beta\, \exp[i(\Delta k' - \tfrac{1}{2}\alpha_2)x_0]\}, \qquad (10)$$

where β is real. Thus, the main effects of this level of absorption of the second harmonic are to reduce the contrast ratio of the Maker fringes and their amplitudes. For the intensity maxima, which will occur for $\Delta k'l = N_{\text{odd}}\pi$, the phase difference between the second harmonic and the fundamental squared emergent from the crystal will be the same as that in the absence of absorption, namely, $\varphi\pm\pi$. Therefore, it is seen that with a 1.06-μ laser, absorption in GaP at the second-harmonic frequency should not introduce any difficulties.

Consider next the case of GaAs, where $\alpha_1 \approx 0$, $\alpha_2 \approx 4.8 \times 10^4$ cm^{-1}, and $\Delta k' \approx 6.4 \times 10^4$ cm^{-1}.[27] The free wave, represented by the second term in Eq. (9), is now absorbed so that Maker SHG fringes are not observed and one has to a good approximation,

$$E_2 = -\frac{8\pi\omega\mathcal{E}_1^2\, d\, \exp[2i(k_1'x_0 - \omega t)]}{c(\Delta k' + \tfrac{1}{2}i\alpha_2)(n_1+1)^2(n_2'+1)}. \qquad (11)$$

Therefore, it is expected that the absorption coefficient

of the second harmonic in GaAs will result in a phase shift φ^a in E_2 due to its effect on the index mismatch, where

$$\varphi^a = \tan^{-1}(-\alpha_2/2\Delta k'), \qquad (12)$$

or $\varphi^a \approx -20°$. In addition to this phase shift, it may be anticipated that d will be complex for GaAs in this wavelength region.[20]

It should be noted that a crystal with $\alpha_2 x_0 \gg 0$, as in the case of GaAs, must be in position A when comparing two crystals since the harmonic wave from crystal A has to be transmitted at least in part through crystal B for the required interference effects to take place.

IV. EXPERIMENTAL RESULTS

Table II gives the absolute signs of the d's determined in these experiments for the transparent crystals, and the experimental values of the φ's for the absorbing crystals. The experimental value of φ, namely, $(\varphi_{ij})_{\text{expt}}$, is defined by

$$(\varphi_{ij})_{\text{expt}} = \varphi_{ij} + \varphi^a, \qquad (13)$$

where the phase shift due to the complex indices of refraction in Eq. (9) is included in φ^a and φ_{ij} is the phase of d. In preparing Table II, it was assumed that the combined effects of absorption were less than 2π.

With every pair of transparent crystals investigated, $P_2(CO_2)$ was at an extremum within the experimental uncertainties of the measurement, namely, $\pm15°$, thereby indicating that for these crystals $\varphi_A - \varphi_B = 0$ or $\pm\pi$. Since the d's are expected to be real for lossless media, these data show that for the transparent crystals $\varphi = 0$ or $\pm\pi$.

The several crystals investigated which absorbed at the second-harmonic frequency were ZnTe, CdSe, CdTe, GaAs, and GaP. In order to convert the relative sign measurements to an absolute basis, platelets of GaP and/or GaAs, with known $+[111]$ directions, were used as crystal A. Comparisons between thin GaP platelets which exhibited Maker fringes and any of the transparent crystals always gave $\varphi_A - \varphi_B = 0$, or π, thereby showing that d_{14} for GaP is also real in this wavelength region. This is not surprising since it was found in these experiments that $\alpha_2 \approx 120$ cm^{-1} for GaP.

Maker fringes were not observed with GaAs due to absorption at 0.53 μ as discussed earlier. The present data with GaAs platelets give a phase $(\varphi_{14})_{\text{expt}} = +15° \pm 15°$ when compared to transparent crystals whose d's were positive. A phase of $+15° \pm 15° \pm \pi$ is ruled out by additional comparisons between GaP and GaAs taking into account that the d's are positive for both GaAs and GaP at 10.6 μ, where they are transparent.[12] Since absorption in GaAs at 0.53 μ is expected to give a phase shift of $\varphi^a = -20°$ due to its effect on the complex index mismatch as shown in Eq. (12), it is concluded that for a 1.06-μ fundamental, $\varphi_{14} = +35° \pm$

20°, or $d_{14}(\text{GaAs}) = d_{14}^0(\text{GaAs}) \exp i(35°\pm20°)$ with respect to the $+[111]$ direction.

In the case of ZnTe(z), the limited refractive index data[28,29] show that φ^a is of the order of 0° to $-10°$, so that d_{ZnTe} is most likely positive with a small positive phase shift due to dispersion, namely, $\varphi_{14}(\text{ZnTe}) \approx 0°$ to $+10°$.

Refractive index data for CdTe(z) indicate that $\alpha_2 \sim 6 \times 10^4$ cm^{-1},[30] which should in turn produce a phase shift φ^a of about $-30°$. Therefore the present data suggest that φ_{14} for CdTe can be either $-\pi+30$, or $\pi+30$.

The data most difficult to analyze for the absorbing crystals are those for CdSe(w). Figure 3 shows a plot of P_2 during the controlled dispersion cycle (described earlier) in a comparison between the d_{33}'s of CdSe and ZnO. The two $+z$ directions were parallel. Since $P_2(\text{CO}_2)$, point B in the figure, is not at an extremum, the relative phase shift is not simply 0 or $\pm\pi$. Analysis of these data in the light of Eq. (7), where φ_{33} for ZnO is $\pm\pi$, shows that $(\varphi_{ij})_{\text{expt}} = \pi - 44° \pm \pi$ for d_{33} in CdSe. The two publications[31,32] which include relevant refractive index data for CdSe are for the present purposes in poor agreement. Furthermore, the present experiments show that α_1 is sufficiently small so that it can be ignored in these experiments, which is in contrast to the published index data.[30] As a result, the present authors are not able to estimate reliably the effects of the complex refractive indices on $(\varphi_{ij})_{\text{expt}}$. On the other hand, it seems reasonable to assume that the effects of absorption will be approximately the same for d_{33} as for d_{31}, in which case one can conclude that d_{31} and d_{33} have opposite signs for CdSe, i.e., their phases differ by $\pm\pi$.

V. COMPARISON WITH THEORY

A. Zinc-Blende Crystals

The electrodynamical bond-charge model developed by Levine[2] predicts that d_{14} is positive for the zinc-blende crystals investigated here, and for those measured earlier as well.[11,12] This theory applies to crystals that are essentially nondispersive, that is, transparent at the laser fundamental and harmonic frequencies. The one transparent zinc-blende crystal measured in this study, ZnSe, is believed to have a positive d_{14}; however, as indicated in Table II, there is no x-ray analysis to relate the absolute structure of the material to its piezoelectric or etching properties. Therefore, it was assumed in preparing Table II that ZnSe has a positive piezoelectric coefficient as do other similar II–VI crystals.[33] In addition, the theory of Phillips and Van Vechten predicts a positive piezoelectric coefficient for ZnSe.[34] Thus, it is concluded that d_{14} is positive for ZnSe and hence in agreement with the theory of Levine

as are the earlier sign determinations for GaP,[11] GaAs, InAs, and GaSb.[12]

The two absorbing zinc-blende crystals measured, ZnTe and CdTe, appear to have positive and negative d's, respectively; however, the effects of dispersion on φ_{14} are not known so that a comparison with extant theories is not now possible.

B. Wurtzite Crystals

Geometrical considerations based on the assumption that the II–VI tetrahedra of the wurtzite structures are undistorted lead to the prediction that for this class of crystals $\pm2d_{31} = \mp d_{33}$,[1,2] which agrees with the relative signs given in Table II except for BeO where d_{31} and d_{33} have the same signs. The sign and magnitude of the ratio d_{33}/d_{31} for BeO remain unexplained within the framework of Levine's theories.[2,6] The difficulty is that the calculation of d_{31} becomes unreliable when there is a near cancellation of the two terms[6] that contribute to the bond nonlinear susceptibility as is the case for BeO. Except for d_{31} for BeO, Levine[6] predicts the observed signs for all the transparent wurtzite crystals measured including the reversal in sign of d_{33} going from CdS to ZnO and BeO. This sign reversal occurs for crystals that contain a first row element, like ZnO, in which case the bond charge is off center.

C. Polar Crystals

The recent theory of Jerphagnon[10] is subjected to a rather stringent test by the present data on polar crystals. Jerphagnon has shown that the vector part of the δ form of the nonlinear tensor that describes SHG, namely, $\delta_{31}+\delta_{32}+\delta_{33}$, is proportional to the spontaneous polarization P_s, where δ (using the full notation) is defined by[35]

$$d_{ijk} = \delta_{ijk}\chi_{ii}{}^{2\omega}\chi_{jj}{}^{\omega}\chi_{kk}{}^{\omega}. \tag{14}$$

The quantities χ_{ll} are the optical susceptibilities $(n_l^2-1)/4\pi$ along the principal index directions l at frequency ω or 2ω as indicated by the superscript. Jerphagnon finds that[10]

$$\delta_{31}+\delta_{32}+\delta_{33} = -(1.0\pm0.3)\times10^{-7}P_s \text{ esu}, \tag{15}$$

where P_s is in μC per cm^2. The sign[7] and magnitude[13] of the coefficient of P_s are determined from experimental data. The crystals LiTaO$_3$, LiNbO$_3$, BaTiO$_3$, and Ba$_2$NaNb$_5$O$_{15}$ have been discussed by Jerphagnon[10,36] and are found to substantiate Eq. (15). The wurtzite crystals ZnO, BeO, and CdS have also been discussed[10,37] by Jerphagnon and are again found to be consistent with Eq. (15) provided that one assumes the direction for P_s in these materials is that which would result from covalent II–VI bonds. It is of interest to note that Eq. (15) requires d_{31} and d_{33} in BeO both be negative as is observed. The above assumption may be questioned

in view of the work of Van Vechten[38] who finds the II–VI bonds for the wurtzite crystals in question to be more ionic than covalent.

The two ferroelastic-ferroelectric molybdates,[39] $Gd_2(MoO_4)_3$ and $Tb_2(MoO_4)_3$ are of special interest since in each case $| d_{31} | \approx | d_{32} |$ and $d_{31}/d_{33} \gg 1$. In particular, $| \delta_{32}/\delta_{33} | \approx | \delta_{31}/\delta_{33} |$ is equal to 69 and 56 for $Gd_2(MoO_4)_3$ and $Tb_2(MoO_4)_3$, respectively.[40] Thus the difference between δ_{31} and δ_{32} must be determined to a precision of about 1% or better to test Eq. (15). The best data on $Gd_2(MoO_4)_3$ show that $\delta_{31}/\delta_{32} = -1.006 \pm 0.014$, and the corresponding quantity for $Tb_2(MoO_4)_3$ is -1.011 ± 0.014. Therefore since δ_{33} is $-$, these data give a negative sign for the sum $\delta_{31}+\delta_{32}+\delta_{33}$ as required by Eq. (15). The magnitudes of these sums are $(-0.23 \pm 0.16) \times 10^{-7}$ and $(-0.26 \pm 0.14) \times 10^{-7}$ esu for $Gd_2(MoO_4)_3$ and $Tb_2(MoO_4)_3$, respectively.[40,41] The value of P_s for both materials is $\sim 0.19 \ \mu C/cm^2$,[39] and therefore in agreement with Eq. (15); however, more precise data are clearly desirable.

The directions and magnitudes of P_s for $LiIO_3$,[9]

$LiGaO_2$,[42] and $LiCHO_2 \cdot H_2O$ [43] are unknown so that comparisons with Eq. (15) are not possible.

D. Other Crystals

The sign of $+$ for d_{11} for left-handed quartz is in agreement with the prediction of Levine when account is taken of the two different ionic radii.[6]

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