product $D(V)P(V)$ was computed using Eqs. (35), (36), and (37) of K1. The theoretical current is practically proportional to this product and the theoretical curve is shown in Fig. 9 normalized to the same peak current as the empirical curves. Clearly, agreement is good up to about the peak voltages, but at higher biases the theoretical curve drops off very much faster than the experimental one. The reasonable conclusion is that the substained experimental currents arise from the presence of band edge tails so that a clean uncrossing of the energy bands does not occur.

Kane has used his band-edge tail theory (K2) to compute the theoretical current-voltage curves for three representative junctions. These junctions cover the range of donor concentrations used in these experiments, namely, 2.5×10^{19}, 4.8×10^{19}, and 1.5×10^{20} cm^{-3}. For all three junctions the acceptor concentration was 2.3×10^{19} cm^{-3}. The true peak voltages found experimentally for these three junctions were 33, 36, and 52 mV. Kane's theory leads to values of 36, 42, and 56 mV, respectively, in good agreement with the experimental values. The empirical curves, $V\exp(-\beta' V)$ with $\beta'=V_p^{-1}$, are compared with the theoretical ones in Fig. 10. For each junction the pairs of curves have been normalized to have the same peak current but the relative magnitudes for the three junctions have no significance. It is clear that in addition to the agreement of peak voltages, the theoretical curves are a good fit to the experimental ones at biases greater than the peak voltage, in contrast to the earlier theory, K1, for undistorted bands. No particular significance can be attached to the slight discrepancies at low biases.

The authors wish to express their appreciation to E. O. Kane for many valuable discussions.

PHYSICAL REVIEW VOLUME 131, NUMBER 1 1 JULY 1963

Mechanism of Second Harmonic Generation of Optical Maser Beams in Quartz

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(Received 18 February 1963)

This paper is concerned with the experimental determination and the interpretation of the relative magnitudes of the two independent coefficients, d_{11} and d_{14}, that appear in the tensor which describes the symmetry of second harmonic generation (SHG) of optical maser beams in quartz. Experimental data on these coefficients aid in determining the physical process involved in optical SHG. Data have been obtained for both ruby (6934 Å) and $CaWO_4$:Nd^{+3}(10 582 Å) unfocused laser beams. These experiments, which failed to give any evidence of SHG due to d_{14}, show that $d_{14}/d_{11}<1/30$ for the ruby laser, and $<1/40$ for the Nd laser. The result $d_{14}\ll d_{11}$ shows that the mechanism involved in SHG in quartz is nearly lossless and dispersionless at the frequencies of the laser beams and their second harmonics. This further shows that in quartz the linear electro-optic effect and optical SHG cannot be due to the same mechanism. It is concluded that optical SHG in this material is due to a high-frequency electronic mechanism.

INTRODUCTION

THERE exists in the literature a fair amount of experimental data[1–4] and theoretical discussion[5–8] on frequency doubling of optical maser beams in quartz. Of particular theoretical interest is the paper by Kleinman[5] which indicates that insight into the mechanism involved in second harmonic generation (SHG) can be obtained from experimental data on the symmetry of the phenomenon. The required data have now been obtained for SHG of the ruby and $CaWO_4$:Nd^{+3} laser beams in quartz. The method by which these data have been determined, and their interpretation in terms of the mechanism responsible for SHG in quartz, are discussed in this paper.

From the point group of quartz, class D_3, it can be shown[1] that the second order polarization, $\mathbf{P}_{2\omega}$, has the form,

$$\mathbf{P}_{2\omega}=\begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ E_yE_z \\ E_xE_z \\ E_xE_y \end{pmatrix}. \quad (1)$$

In Eq. (1), $\mathbf{P}_{2\omega}$ is the part of the dielectric polarization that varies with time at twice the laser frequency ω, E_i are the optical electric field components in the medium at frequency ω, and d_{ij} are the nonlinear coefficients. There has been some speculation concerning the magni-

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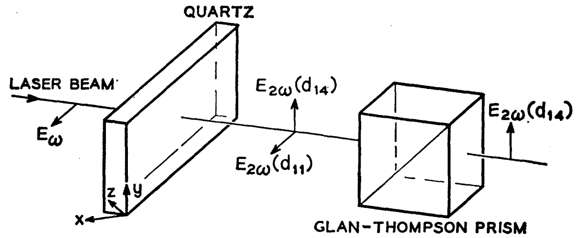

FIG. 1. Schematic drawing showing the orientation of the quartz sample with respect to the polarized laser beam for separating the second harmonic light waves due to the two nonlinear coefficients d_{11} and d_{14}.

tude of d_{14} compared to d_{11}.[5,7] Kleinman,[5] who was the first to study the problem, used a thermodynamic argument to show that if a lossless and dispersionless mechanism is responsible for SHG, e.g., a high frequency electronic mechanism, additional symmetry requirements beyond those resulting from the crystal symmetry may apply to some crystals. The additional symmetry requirements, which will be called the Kleinman symmetry conditions (KSC), do not apply to the three ionic mechanisms[5] that can result in SHG, namely, anharmonicity, second-order electric moments, and Raman scattering. With respect to the case under consideration in the present paper, the KSC give,

$$d_{14}=d_{25}=d_{36}, \qquad (2)$$

which for quartz requires that $d_{14}\equiv 0$. Armstrong *et al.*[6] have shown that the KSC are a special case of their more general symmetry relations for nonabsorbing media. In particular, the KSC, e.g., Eq. (2), are strictly correct only for nondispersive media and are, therefore, regarded as an approximate result. However, in the case of quartz, for example, where dispersion is small in the spectral region of the optical maser frequencies and their second harmonics, one might expect the KSC to be a good approximation.

In all the experimental studies of SHG in quartz reported to date,[1–4] there has been no attempt to observe a contribution from the d_{14} coefficient. The symmetry requirements given in Eq. (2) applied to piezoelectric crystals in classes D_4 and D_6 result in all $d_{ij}=0$. The only test of Eq. (2) reported to date is that involving guanidine carbonate,[4] a crystal in class D_4. Out of about fifteen piezoelectric crystals investigated for SHG with the ruby laser, only guanidine carbonate failed to exhibit an observable harmonic. All the other crystals tested possess symmetries which permit SHG even with the KSC. Therefore, the negative result for guanidine carbonate supports the nondispersive, lossless, mechanism for SHG.

Recently Franken and Ward[7] have estimated d_{14}/d_{11} for the ruby laser (6934 Å) interacting with quartz and concluded that this ratio could be of order $\frac{1}{3}$. This nonzero value of d_{14}/d_{11} originates in the quantum-mechanical formulation described by Franken and Ward from the small amount of dispersion, e.g., approximately 2% for the ruby laser, that occurs between the fundamental and the second harmonic frequency. If the same procedure is used to estimate d_{14}/d_{11} for the $CaWO_4$:Nd^{+3} laser (1.06 μ), one obtains d_{14}/d_{11} of order $\frac{1}{10}$. A ratio of d_{14}/d_{11} of the order of $\frac{1}{10}$ or larger would be easy to detect experimentally.

EXPERIMENTAL

Figure 1 shows a schematic drawing of the essential components in the experimental arrangement. The quartz crystal, 2 mm thick, has the y axis in the plane of the plate while the x (binary) and z (trigonal) axes each make an angle of 45° with respect to the normal to the plate. The unfocused laser beam, polarized with the electric vector in the quartz x-z plane, is directed along the plate normal. Under these conditions, Eq. (1) becomes

$$\mathbf{P}_{2\omega}=d_{11}E_x^2\mathbf{X}_0-d_{14}E_xE_z\mathbf{Y}_0, \qquad (3)$$

where $\mathbf{X}_0$ and $\mathbf{Y}_0$ are unit vectors along the quartz x and y axes, respectively. Thus, with the aid of a polarizing element, contributions to the second harmonic from d_{11} and d_{14} can be separated and compared.

The discussion given above neglects the influence of the optical activity of quartz.[9] This effect could, for example, produce a second harmonic signal polarized along the y axis due to optical rotation of the plane of polarization of a second harmonic wave polarized in the xz plane. Since the rotary power is largest at the shortest wavelengths, only the influence of optical activity on the second harmonic light need be considered. The effects due to optical activity have been calculated for the geometry shown in Fig. 1 and are found to be negligible in so far as the present results are concerned. In the case of the $CaWO_4$:Nd^{+3} second harmonic, the maximum amplitude (for a crystal of optimum thickness) of the wave polarized along the y axis produced by the effects of optical activity on a second harmonic wave polarized in the xz plane, will be about 2×10^{-5} times the amplitude of the light wave polarized in the xz plane. The corresponding figure for the ruby laser is about 6×10^{-5}. It is worthwhile noting that this effect due to optical activity can be eliminated completely in quartz if one uses a sample oriented so that the beam direction in the crystal is at 56° 10′ to the optic axis.[9]

RESULTS AND DISCUSSION

Preliminary data obtained with the laser beams at normal incidence to the sample indicated that any contribution from d_{14} was below the noise level of the detection system. However, to make quantitative comparisons of nonlinear coefficients, it is necessary to consider the interference effects that occur between the second order polarization wave (forced wave[8]) and the free

[9] See, for example, J. F. Nye, *Physical Properties of Crystals* (Clarendon Press, Oxford, England, 1960).

second harmonic light wave.[2,6] Maker *et al.*[2] have demonstrated the existence of this effect in quartz. The interference, which arises from a combination of anisotropy and dispersion, produces a second harmonic wave whose amplitude varies in a periodic manner along the beam direction from zero to some maximum value. For the case under study, the intensities of the second harmonic waves as a function of the distance η in the crystal can be represented by

$$I_{11} \propto d_{11}^2 l_{11}^2 E_x^4 \sin^2\theta \sin^2(\pi\eta/2l_{11}), \quad (4)$$

and

$$I_{14} \propto d_{14}^2 l_{14}^2 E_x^2 E_z^2 \sin^2(\pi\eta/2l_{14}). \quad (5)$$

In these expressions, θ is the angle between the beam direction and the optic axis, and l is the coherence length.[1,7] The coherence length is given by $l=\lambda_1/4\Delta n$, where λ_1 is the free space wavelength of the fundamental, and Δn is the difference between the indices of refraction for the second harmonic and fundamental light waves. In order to ascertain that a contribution from d_{14} was not fortuitously absent in the preliminary data due to these interference effects, and that any intensities observed were representative of the maxima of the second harmonic light waves, both output polarizations were observed as the crystal was rotated about the y axis. This rotation changes the path length of the beam in the crystal so that the periodic variation of the second harmonic is observed. For both lasers, the d_{11} contribution exhibited the characteristic interference effects described by Eq. (4). The coherence lengths calculated from the experimental data, $l_{11}=20\ \mu$ for the Nd laser, and $l_{11}=7\ \mu$ for the ruby laser, are in agreement with those estimated from index of refraction data.[10] No contribution due to d_{14} was observed. When these data are analyzed with the aid of Eqs. (4) and (5), it is found that $d_{14}/d_{11}<1/30$ for the ruby laser and $<1/40$ for the $CaWO_4$:Nd^{+3} laser.

Thus, it is clear that any contribution to the second harmonic of these optical maser beams due to d_{14} is at least three orders of magnitude smaller than that due to d_{11}. The experimental result that $d_{14} \ll d_{11}$ is in agreement with the additional symmetry requirements described by Kleinman for a lossless and dispersionless mechanism for SHG. Therefore, in the case of quartz, a high frequency electronic mechanism is the important physical process involved in the generation of the second harmonic. However, as discussed by Kleinman,[5] the fact that the two electro-optic coefficients for quartz are of the same magnitude indicates that an ionic mechanism, and not a high frequency electronic process, is involved in the linear electro-optic effect in this material. It, therefore, appears that for quartz, SHG and the linear electro-optic effect are due to different physical processes. In support of this statement, it should be noted that the coefficients which describe the quantitative aspects of SHG[8] and the linear electro-optic effect[7,10] differ by about two orders of magnitude.

The estimates of (d_{14}/d_{11}) made by Franken and Ward[7] seem to be too large. It appears to the present author that the method employed to estimate the effects due to dispersion may only be valid for comparing nonlinear coefficients which become equal in the absence of dispersion, i.e., in the limit that 2ω can be considered a low frequency. Franken and Ward show that d_{14}, d_{25}, and d_{36} become equal as the laser frequency approaches zero, which should be the case if the theory is correct. However, it is certainly not required that $d_{11} \rightarrow d_{14}$ as $\omega \rightarrow 0$ and, therefore, d_{11} and d_{14} cannot, in general, be compared at optical frequencies by just considering the frequency-dependent parts of the theoretical expressions for the nonlinear coefficients. In view of these remarks, it would seem that a more meaningful test of this method for estimating the effects of dispersion on the KSC would be to measure and compare d_{14} and d_{36} in KDP. For this case, Franken and Ward estimate that d_{14} and d_{36} could differ by of the order of 30%.

Note added in proof. Recent data on KDP (to be published) show that for both the Nd and ruby lasers, the coefficients d_{14} and d_{36} are equal to within 5%.

Franken and Ward (private communication) have recently refined the order-of-magnitude estimates, quoted in Ref. 7, for the coefficient ratios in quartz and KDP with the result that the ratios should be about an order of magnitude less than stated earlier. One of the important changes in the calculation is that the effective frequency which determines the dispersion of the coefficients is now assumed to be the frequency which describes the optical dispersion with a Clausius-Mosotti type expression, rather than the frequency of the absorption edge which was used previously.

ACKNOWLEDGMENTS

The author would like to acknowledge important contributions to various phases of this work by E. A. Wood, W. L. Bond, A. Savage, and especially D. A. Kleinman. In addition, several discussions with Professor P. A. Franken on the content of the paper resulted in an improved manuscript.

[10] See, for example, *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957) Sec. 6.