Experimental Verification of the Laws for the Reflected Intensity of Second-Harmonic Light*

R. K. CHANG AND N. BLOEMBERGEN
Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts
(Received 1 November 1965)

The intensity of the second-harmonic light generated in reflection from piezoelectric crystals of GaAs has been measured as a function of the angle of incidence of the primary ruby- or neodymium-glass-laser beam. The second-harmonic intensity has been measured for various crystallographic orientations of the GaAs mirror surface and for different directions of polarization. The results verify the theoretical predictions of Bloembergen and Pershan. In particular, the existence of a "Brewster angle" for second-harmonic reflection, with the harmonic electric field in the plane of reflection, has been observed.

I. INTRODUCTION

THE behavior of light waves at the boundary of a nonlinear optical medium has been analyzed theoretically by Bloembergen and Pershan.[1] A parametrically generated nonlinear polarization at a combination frequency $\sum_i(p_i\omega_i)$, where p_i is a positive or negative integer and ω_i is a frequency contained in the incident light beams, radiates a reflected ray at this combination frequency in addition to the transmitted rays. Quantitative expressions for the direction, polarization, and intensity of these parametrically generated reflected light waves have been derived by BP. The second-harmonic generation in reflection was first observed by Ducuing.[2,3] Both the directional and the polarization properties of the second harmonic reflected from III-V semiconductor mirrors, have been verified. In the present paper we report on the dependence of the intensity of the reflected second harmonic as a function of the angle of incidence and the crystallographic orientation of the nonlinear mirror surface. The results lead to a further detailed verification of those equations in BP, which may be regarded as generalizations to the nonlinear case of the well-known Fresnel formulas for linear optical reflection.

These equations have been used at one particular angle of incidence to measure the nonlinear susceptibility of several semiconductor compounds relative to that of potassium dihydrogen phosphate (KDP).[4,5] A detailed experimental verification of the correctness of the equations of BP as a function of the angle of incidence is therefore important. One particular predicted feature is the existence of a "Brewster angle" in the case that the nonlinear polarization lies in the plane of reflection. This phenomenon has been observed and is described in the final section of this paper.

Crystals with $\bar{4}3m$ (T_d) symmetry are particularly well suited for the present purpose, because they are optically isotropic as far as their linear properties are concerned. Since the dielectric constants $\epsilon(\omega)$ and $\epsilon(2\omega)$ figure prominently in the equations for nonlinear reflection, great simplification is obtained if $\epsilon(\omega)$ and $\epsilon(2\omega)$ can be treated as scalar quantities. The explicit formulas in BP are only valid for this cubic class. The second-harmonic polarization has the following three components with respect to the cubic crystallographic axes (x,y,z):

$$\begin{aligned} P_x^{\mathrm{NLS}}(2\omega)&=\chi_{14}^{\mathrm{NL}}E_y^T(\omega)E_z^T(\omega)\,,\\ P_y^{\mathrm{NLS}}(2\omega)&=\chi_{14}^{\mathrm{NL}}E_z^T(\omega)E_x^T(\omega)\,,\\ P_z^{\mathrm{NLS}}(2\omega)&=\chi_{14}^{\mathrm{NL}}E_x^T(\omega)E_y^T(\omega)\,. \end{aligned} \tag{1}$$

The components $E_x^T(\omega)$, $E_y^T(\omega)$, and $E_z^T(\omega)$ are those of the transmitted laser beam. They can be expressed in terms of the incident laser field by means of the linear Fresnel formulas, for each angle of incidence, polarization and crystallographic orientation. The equations (4.6) and (4.13) of BP then give the reflected second-harmonic field in terms of $\mathbf{P}^{\mathrm{NLS}}(2\omega)$. These equations are reproduced here for the sake of convenience. The reflected second-harmonic amplitude polarized normal to the plane of reflection is given by

$$E_\perp^R(2\omega)=\frac{-4\pi P_\perp^{\mathrm{NLS}}\sin^2\theta_T\sin\theta_S}{\sin(\theta_R+\theta_T)\sin(\theta_S+\theta_T)\sin\theta_R}. \tag{2}$$

For the case of one incident light beam in vacuum (or air) with an angle of incidence θ_i, the angles in this equation are determined by the relations

$$\theta_R=\theta_i,\ \sin\theta_S=\epsilon^{-1/2}(\omega)\sin\theta_i,\ \sin\theta_T=\epsilon^{-1/2}(2\omega)\sin\theta_i. \tag{3}$$

The component of the reflected harmonic amplitude in the plane of reflection is given by

$$E_{11}^R(2\omega)=\frac{4\pi P_{11}^{\mathrm{NLS}}\sin\theta_S\sin^2\theta_T\sin(\alpha+\theta_T+\theta_S)}{\epsilon_R\sin\theta_R\sin(\theta_T+\theta_S)\sin(\theta_T+\theta_R)\cos(\theta_T-\theta_R)}. \tag{4}$$

* This research was supported jointly by the U. S. Office of Naval Research and by the Advanced Research Projects Agency. A preliminary account of these results was given in the Bull. Am. Phys. Soc. 10, 438 (1965). This material is also described in Chap. 2 of a Ph.D. thesis by R. K. Chang, Harvard University, 1965 (unpublished).

[1] N. Bloembergen and P. S. Pershan, Phys. Rev. **128**, 606 (1962). This paper will henceforth be referred to as BP.

[2] J. Ducuing and N. Bloembergen, Phys. Rev. Letters **10**, 474 (1963).

[3] N. Bloembergen and J. Ducuing, Phys. Letters **6**, 5 (1963).

[4] N. Bloembergen, R. K. Chang, J. Ducuing, and P. Lallemand, *Proceedings of the Seventh International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 121.

[5] R. K. Chang, J. Ducuing, and N. Bloembergen, Phys. Rev. Letters **15**, 415 (1965).

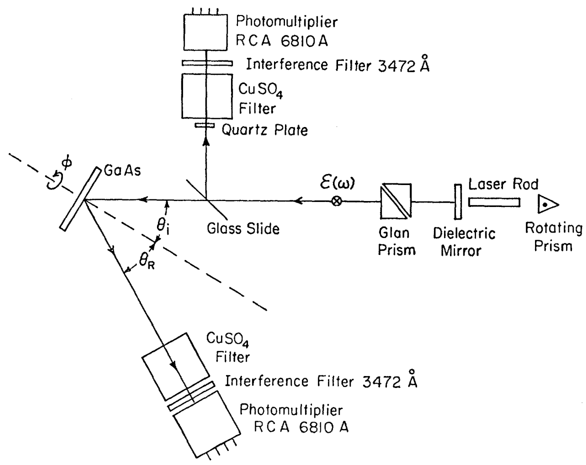


FIG. 1. Experimental arrangement for the verification of the laws for nonlinear optical reflection.

In this equation P_{11}^{NLS} is the component of the nonlinear polarization in the plane of reflection, and $\alpha+\theta_S$ is the angle between P_{11}^{NLS} and the surface normal. All equations retain their validity for complex values of θ_S and θ_T. For nonlinear reflection measurements it is an advantage if $\epsilon(\omega)$ and/or $\epsilon(2\omega)$ are complex. The linear absorption at ω or 2ω assures that the transmitted second-harmonic intensity does not build up to much larger values. The measurement of the reflected intensity is therefore not influenced by backscattering of transmitted beams.

All measurements to be reported in this paper were carried out with GaAs mirrors. In Sec. II the experimental techniques are described. The experimental results are presented and compared with theory in Sec. III. The special case of Brewster's angle is discussed in Sec. IV.

II. EXPERIMENTAL TECHNIQUE

A. Crystal Preparation

The mirror surfaces of all GaAs crystals, which had typical dimensions of $1\times0.5\times0.1$ cm^3 and were purchased from the Monsanto Chemical Company, were prepared in the following manner. One face of the crystal is first coarsely polished with 100-μ abrasive. This is then followed in sequence by 1-μ Linde C, 0.3-μ Linde A, and 0.1-μ Linde B abrasives. The depth of the damaged layer for different III-V compounds has been reported by Gatos[6] to be less for crystals with larger energy gap. Thus extrapolating from that work, the damaged layer for GaAs after using 0.1-μ abrasive should be about 0.025 μ. The far-field optical reflecting quality of a crystal after 0.1-μ abrasive polishing is good throughout a large central portion of the crystal. The edges are found to be somewhat rounded. After the 0.1-μ polishing the crystal is mildly etched. If the crystal is strongly etched, the surface would be very wavy, causing the second-harmonic beam to be spatially diffused. This problem is particularly acute at large incident angles (i.e., $\theta_i>50°$). The reflected ray directions must always be confined to an angular spread less than 4° to avoid systematic errors. The etching solution used for the III-V compounds are mixed according to Gatos *et al.*[7] The (1,1,0) mirror may also be obtained by cleavage. The first and foremost criterion the polished-etched crystals must satisfy is that the induced nonlinear polarization satisfies Eqs. (1). The nonlinear susceptibility must possess the bulk symmetry properties of a single crystal. Our experimental results are independent of doping of the GaAs crystals.

B. Apparatus and Experimental Method

The experimental arrangement is shown in Fig. 1. It consists of a ruby laser operated in a Q-switched condition by means of a rotating prism. The laser output lasts about 30×10^{-9} sec and its output energy is typically 0.05 J. The laser light is first linearly polarized by a Glan polarizer, and is subsequently incident on the semiconductor mirror whose nonlinear optical properties are under investigation. The angle of incidence can be varied between 20° to 70°, with an accuracy of $\pm15'$, by rotating the sample holder about its vertical axis. The sample holder is further designed so that the crystal can be rotated about its face normal. This is particularly useful when one wishes to compare the second-harmonic intensity generated when different crystalline axes are made parallel to the laser polarization. This rotation is reproducible within $\pm1°$.

As the reflected laser beam and the second-harmonic light come out in the same direction in air, $\theta_R=\theta_i$, the fundamental must be filtered from the harmonic light. This is accomplished by allowing the reflected beam to traverse a 2-in. cell containing $CuSO_4$ solution followed by an interference filter which is peaked at 3472 Å, the harmonic wavelength. After these filterings, the second-harmonic signal is then incident on an RCA 6810 A photomultiplier, and its output is displayed on the oscilloscope screen and photographed on Polaroid film. The $CuSO_4$ cell, interference filter, and photomultiplier system are mounted on an arm which can be rotated about the center of the sample holder. Thus for every different angle of incidence, the arm can be rotated so that its axis is made parallel to the reflected-ray direction. Before the polarized laser beam encounters the nonlinear mirror, it traverses two beam splitters, consisting of microscope slides. The first slide reflects about 10% of the laser beam onto an RCA 917 photodiode, whose output is used to trigger the oscilloscope which is set on the single sweep mode. The 10% of the laser

[6] H. C. Gatos, M. C. Lavine, and E. P. Warekois, J. Electrochem. Soc. 108, 645 (1961).

[7] H. C. Gatos and M. C. Lavine, Lincoln Laboratory Technical Report No. 293 (unpublished).

beam reflected by the second microscope slide is used for monitoring the primary beam.

Our high-power laser operates in several modes (both in frequency and in space), whose amplitude and phase are random variables. The laser output does not have perfect spatial and temporal coherence. When dealing with a nonlinear effect like second-harmonic generation, one does not get a perfect one-to-one correspondence between the amplitudes of the fundamental and harmonic pulses.[8] There is, however, a nonrandom one-to-one correspondence between two nonlinear processes of the same order, obtained from the same laser pulse by means of a partially reflecting mirror. Ten percent of the laser beam reflected by the second microscope slide is incident on a Z-cut quartz platelet. The second-harmonic is generated in the quartz as the laser light traverses it. The latter is filtered out by a $CuSO_4$ solution cell and an interference filter peaked at the harmonic wavelength, while the second-harmonic is detected by another RCA 6810 A photomultiplier. The signal from that is also directly connected to the dual-beam oscilloscope. Thus for every firing of the laser, the second-harmonic generated by reflection from the semiconductor mirror is compared with the second-harmonic generated by transmission from a quartz platelet. The fluctuations in the ratio of these two signals from individual firings of the laser is typically between 5–10%. Each experimental point shown in Figs. 2 through 5 is an average of 5 to 10 laser firings, improving the accuracy of the average to an error of about 3%.

Quartz is used in the monitoring arm, rather than KDP, because its surface does not deteriorate with time. The Z cut is chosen mainly because of the convenience in not having to worry about the orientation of the laser polarization with respect to the crystalline axis. If the Z axis is normal to the platelet, the second-harmonic intensity from the quartz is proportional to

$$I(2\omega) \propto (\chi_{(2\omega)}{}^{\mathrm{NL}})^2 (E^4{}_{x(\omega)} + 2E^2{}_{x(\omega)} E^2{}_{y(\omega)} + E^4{}_{y(\omega)}) \propto (\chi_{(2\omega)}{}^{\mathrm{NL}})^2 E^4{}_{(\omega)}.$$

Here $E_{x(\omega)}$ and $E_{y(\omega)}$ are the projection of the laser field $E_{(\omega)}$ on the X and Y axes of the quartz crystal. The second-harmonic intensity is not changed when one rotates the quartz about the Z axis. Another advantage of using a Z cut as the normal of the platelet is that the crystal is far from the phase-matching condition. Thus accidental misalignment of the monitoring system would not affect the second-harmonic conversion by a noticeable amount.

The laser light incident on the semiconductor mirror is slightly focused, not because more fundamental intensity is needed, but to make the size of the laser spot less than the area of the crystal at the largest angle of incidence.

[8] J. Ducuing and N. Bloembergen, Phys. Rev. **133**, A1473 (1964).

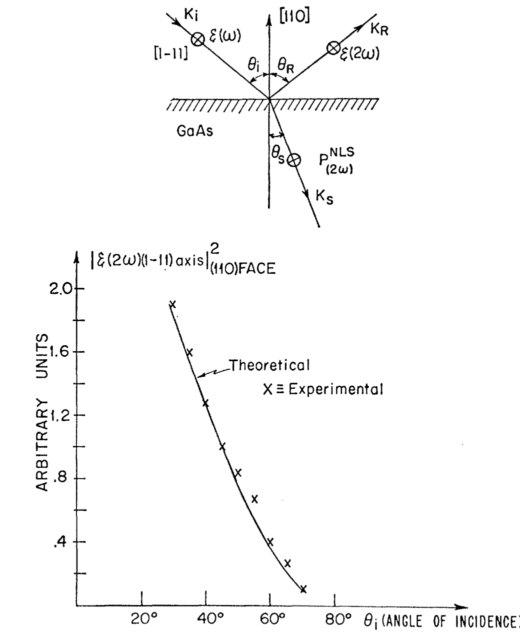


FIG. 2. The variation of the second-harmonic intensity, generated in reflection from a GaAs mirror, as a function of the angle of incidence of the laser beam at the fundamental frequency. Details of the geometry are shown at the top.

The quality of the surface should be such that the nonlinear polarization is described by Eqs. (1), which are valid for the symmetry of the bulk crystal. The reflected harmonic intensity is generated in a layer near the surface, a few hundred angstroms thick, corresponding to the absorption depth for the second-harmonic light in GaAs. In this layer the cubic axes of volume symmetry of the single crystal must be well defined. It follows from Eqs. (1) that no second-harmonic intensity should be generated, if the electric field at the fundamental laser frequency is polarized along a cubic axis. The experimental criterion for an acceptable surface was that the second-harmonic intensity generated with the laser field parallel to the (1,1,0) direction should be at least twenty times larger than with the laser field along the (1,0,0) axis.

III. EXPERIMENTAL RESULTS

The first experiment designed to examine the variation of second-harmonic intensity from the semiconductor mirror as a function of incident angle for a given laser intensity utilizes the geometry shown in Fig. 2. The nonlinear mirror is a [1,1,0] face of a GaAs single crystal. The $(1, -1, 1)$ direction of the crystal is aligned parallel to the laser polarization. The resulting nonlinear source polarization will then also be in the $(1, -1, 1)$ direction, or perpendicular to the plane of reflection for all angles of incidence. This angle θ_i is varied from 30° to 70° at 5° intervals. For each angle of incidence, the arm which contains the filtering and photomultiplier systems is aligned so that its axis is made parallel to the direction of the reflected ray.

The experimental data, for the second-harmonic intensity, proportional to $|E_\perp(2\omega)|^2$, are shown as crosses in Fig. 2. The solid line represents the theoretical curve. The nonlinear polarization in this geometry is given by

$$P_\perp^{\rm NLS}=3^{-1/2}\chi_{14}^{\rm NL}(2\omega)E_i^2(\omega)\times[2\sin\theta_S\cos\theta_i/\sin(\theta_i+\theta_S)]^2. \quad (5)$$

The last factor is the Fresnel factor for transmission of the incident laser beam $E_i(\omega)$ into the medium. The values of θ_S and θ_T are determined by Eq. (3) from the known complex values for the linear dielectric constant, $\epsilon(\omega)$ and $\epsilon(2\omega)$. When Eq. (5) is substituted into Eq. (2) and the experimental data of Phillip and Ehrenreich[9] are used for $\epsilon(\omega)$ and $\epsilon(2\omega)$, satisfactory agreement between theory (drawn curve) and experimental points in Fig. 2 is obtained. Our results show that, at the laser intensities used in these experiments the index of refraction is not appreciably altered by the creation of electron-hole pairs. The angular dependence of the second-harmonic intensity is dominated by the angular variation of the linear Fresnel factor,

$$|2\sin\theta_S\cos\theta_i/\sin(\theta_i+\theta_S)|^4.$$

A more meaningful test for the typical factors of the nonlinear theory, appearing in Eqs. (2) and (4), can be obtained by measuring the ratio of the second-harmonic intensities with the laser polarization perpendicular to the plane of incidence, but parallel to different crystallographic orientations in the mirror plane. The linear Fresnel factor is eliminated in this ratio, because $\epsilon(\omega)$ is a scalar in this cubic material and does not depend on crystal orientation.

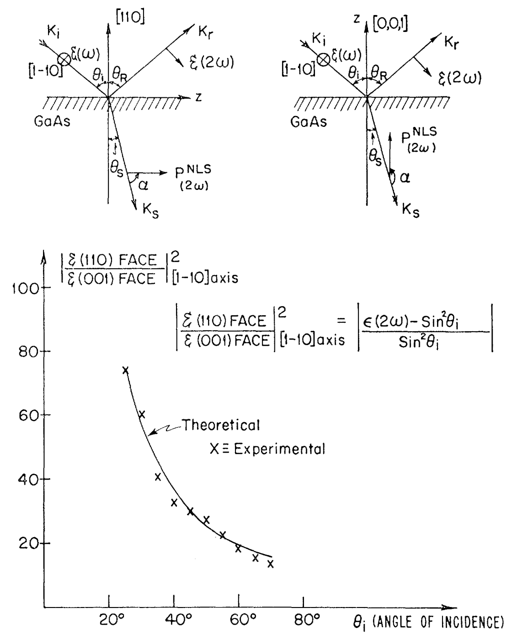


FIG. 4. The ratio of the second-harmonic intensities for two geometries shown at the top, as a function of the angle of incidence. The Fresnel transmission factor for the laser beam is eliminated in the comparison of two different crystallographic orientations of the mirror face.

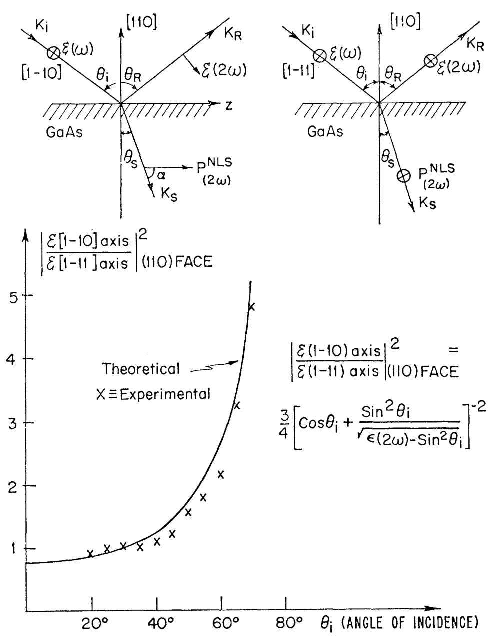


FIG. 3. The ratio of the second-harmonic intensities for two geometries shown at the top, as a function of the angle of incidence. The Fresnel transmission factor for the laser beam is eliminated in this comparison of two different harmonic polarizations.

[9] H. R. Phillip and H. Ehrenreich, Phys. Rev. **129**, 1550 (1963).

The two diagrams at the top of Fig. 3 illustrate the two geometries. The incident laser beam has an electric field normal to the plane of incidence and the mirror surface is a [1,1,0] cut in both cases. In one case the incident electric field is parallel to the (1, 1, -1) direction in the plane of the mirror. This is the geometry of Fig. 2 and the second harmonic is perpendicular to the plane of reflection. In the second case the incident electric field is parallel to the (1, -1, 0) direction in the plane of the mirror. The second-harmonic polarization in this case is given by

$$P_{11}^{\rm NLS}=\tfrac{1}{2}\chi_{14}^{\rm NL}(2\omega)E_i^2(\omega)\times[2\sin\theta_S\cos\theta_i/\sin(\theta_i+\theta_S)]^2. \quad (6)$$

The reflected harmonic field in this case is given by Eq. (4) with $\alpha+\theta_S=\frac{1}{2}\pi$. The ratio of the second-harmonic intensity, for the same incident laser beam, in these two cases is consequently given by

$$\left|\frac{E_{11}(1,-1,0)}{E_\perp(1,-1,1)}\right|^2_{[1,1,0]\text{ face}}=\frac{3}{4}\left|\cos\theta_i+\frac{\sin^2\theta_i}{[\epsilon(2\omega)-\sin^2\theta_i]^{1/2}}\right|^2. \quad (7)$$

Experimentally, at each angle of incidence, five to ten laser firings were made for one geometry. Then the mirror was turned around its own normal, and an equal number of firings was made in the other geometry. The experimental results for the ratio of the second-harmonic intensities are compared with the theoretical curve, given by Eq. (7), in Fig. 3. The agreement of the experimental ratios with the angular dependence is striking. This proves two important points. First, the theory is correct for the angular dependence of the second-harmonic generation when the P^{NLS} is perpendicular or parallel to the plane of reflection. Second, the crystal behaves as an ideal nonlinear mirror, within the accuracy of the measurements. That is, although the second harmonic is generated in a layer a few hundred angstroms thick, just below the surface, that layer still has the symmetry of the bulk. Furthermore, it has about the same linear dielectric constant as that of the bulk material.

For the same angle of incidence, the ratio of second-harmonic intensities from two mirror planes with different crystallographic orientations is also independent of the transmission of the laser into the nonlinear material. This ratio becomes very simple when the laser polarization is parallel to the (1, −1, 0) direction in a [1,1,0] face and in a [0,0,1] face, respectively. The nonlinear polarizations for both these cases are in the plane of reflection. In particular, the nonlinear polarization for the [1,1,0] face crystal is parallel to the surface with $\alpha+\theta_S=\frac{1}{2}\pi$ while the nonlinear polarization for the [0,0,1] face crystal is normal with $\alpha+\theta_S=\pi$. Substituting these angles into Eq. (4), the ratio of second-harmonic intensities as a function of incident angle reduces to

$$\left|\frac{E_{(1,1,0)\text{ face}}}{E_{(0,0,1)\text{ face}}}\right|^2_{(1,-1,0)\text{ axis}}=\left|\frac{\epsilon(2\omega)-\sin^2\theta_i}{\sin^2\theta_i}\right|. \qquad (8)$$

Experimentally, the following is done. At each incident angle, after the intensity of second-harmonic from a [1, −1, 0] face mirror is determined, a [0,0,1] face GaAs mirror is placed in the sample holder. The

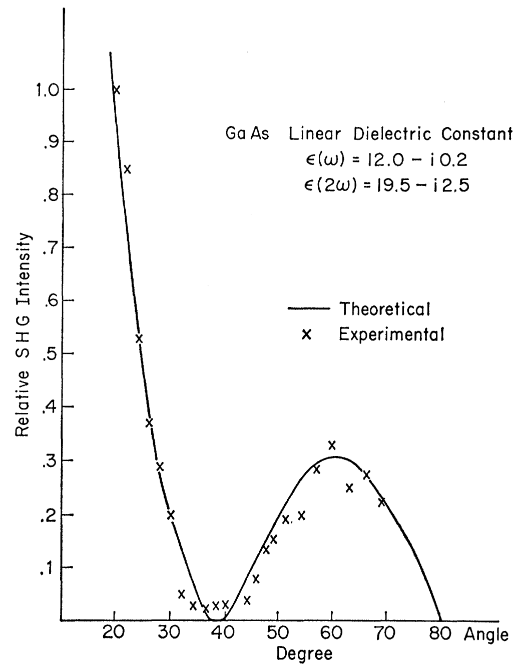
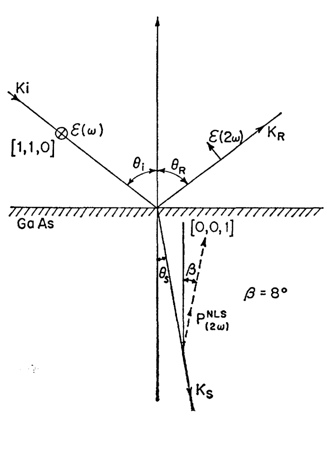


FIG. 6. The second-harmonic intensity, for the geometry of Fig. 5, as a function of the angle of incidence for a neodymium-glass-laser beam.

intensity of second harmonic is again determined with the laser field parallel to the (1,1,0) axes. This ratio is plotted in Fig. 4, and compared with the theoretical result of Eq. (8) represented by the solid curve.

Two interesting features should be mentioned with regard to Fig. 4. First, one can extract from the experimental results the value of $\epsilon(2\omega)$. The extracted result for GaAs at the second-harmonic wavelength of ruby is consistent with that found by Phillip and Ehrenreich.[9] Second, the ratio of the two intensities increases rapidly as the angle of incidence decreases. It is clear that, when $P^{NLS}(2\omega)$ is normal to the surface, it cannot radiate in this normal direction. For $\theta_i\rightarrow 0$ and $\alpha+\theta_S=\pi$ the second-harmonic intensity must vanish. This is a special degenerate case of a Brewster angle for second-harmonic generation.

FIG. 5. The geometry of the GaAs mirror and the polarizations, used in the verification of Brewster's angle for second-harmonic generation.



IV. BREWSTER ANGLE FOR SECOND-HARMONIC GENERATION

A more rigorous test of the theory may be obtained by using the geometry shown in Fig. 5. The mirror surface of the GaAs crystal contains the (1,1,0) face diagonal and its normal makes an angle $\beta=8°$ with the crystallographic (0,0,1) axis. The incident laser beam is polarized with the electric field $\mathbf{E}(\omega)$ normal to the plane of incidence and parallel to the (1,1,0) direction. In this manner the nonlinear polarization is always parallel to the Z axis and always makes an angle of 8° with the mirror normal, regardless of the angle of incidence θ_i. The second-harmonic reflected light is

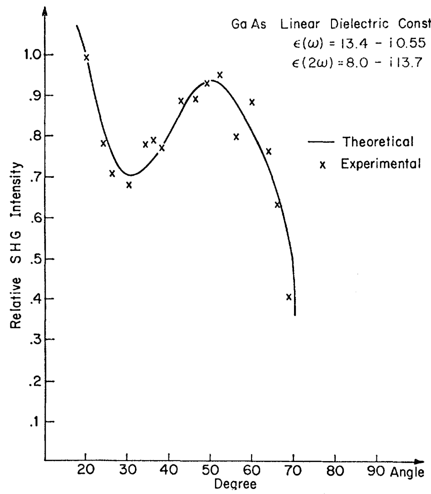


FIG. 7. The second-harmonic intensity, for the geometry of Fig. 5, as a function of the angle of incidence for a ruby-laser beam.

always polarized with the electric field in the plane of reflection. Consequently, Eq. (4) must be used with $\alpha+\theta_S=\pi-8°$. The equation shows that for $\theta_T=8°$, or for $\sin\theta_i=\epsilon^{1/2}(2\omega)\sin\theta_T=\epsilon^{1/2}(2\omega)\sin 8°$, the reflected harmonic intensity must vanish. As was pointed out by BP the second-harmonic polarization source cannot radiate in the direction $\beta=8°$ *inside* the linear dielectric medium, which after refraction would give rise to the reflected ray in the direction θ_R. This behavior has been confirmed experimentally as shown by the data in Fig. 6. The theoretical curve, predicted by Eq. (4), is shown for comparison, There is a good fit, if the experimental values of Phillip and Ehrenreich[9] are used, $\epsilon(\omega)=12.0-i0.2$ and $\epsilon(2\omega)=19.5-i2.5$ appropriate for the fundamental and second-harmonic frequency of a neodymium glass laser. The vanishing of the reflected intensity for $\theta_R=38°$, corresponding to the angle $\theta_T=\beta=8°$ inside the crystal, is quite marked, although not as complete as predicted by the theory. The remaining small experimental signal may well be caused by incoherent recombination radiation as its frequency and angular distribution was considerably broader than that measured in other directions.

The data taken with a ruby laser in the same geometry, which historically preceded the data at the neodymium frequency, are shown in Fig. 7. Although there is a pronounced dip near $\theta_R\approx 30°$, the second-harmonic intensity does not go to zero. The reason is that the dielectric constant of GaAs at the ruby second-harmonic frequency has a large imaginary part, $\epsilon(2\omega)=8.0-i13.7$. Therefore, no real Brewster angle, which must satisfy $\sin\theta_R=\epsilon^{1/2}(2\omega)\sin 8°$, can be found. The theoretical expressions remain valid, however, for complex dielectric constants and complex angles. The theoretical prediction, represented by the solid curve in Fig. 7, gives again excellent agreement with the experimental points. In this case of complex $\epsilon(2\omega)$ the planes of constant phase and constant amplitude do not coincide, and no zero in the reflected intensity can develop. This is also well known in the case of linear reflection from metallic surfaces.

V. CONCLUSION

The second-harmonic generation in reflection from a crystal with $\bar{4}3m$ symmetry verifies the theory of BP. The direction, polarization, and intensity of the reflected harmonic rays depends in the predicted manner on the angle of incidence of the primary laser beam and on the crystallographic orientation of the mirror surface. The surface layer about 200 Å thick of suitably prepared GaAs crystals exhibits the full volume symmetry of the crystal. The analogs of Fresnel's equations for the nonlinear case have been verified.