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Light Waves at the Boundary of Nonlinear Media

N. Bloembergen and P. S. Pershan
Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts
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Solutions to Maxwell's equations in nonlinear dielectrics are presented which satisfy the boundary conditions at a plane interface between a linear and nonlinear medium. Harmonic waves emanate from the boundary. Generalizations of the well-known laws of reflection and refraction give the direction of the boundary harmonic waves. Their intensity and polarization conditions are described by generalizations of the Fresnel formulas. The equivalent Brewster angle for harmonic waves is derived. The various conditions for total reflection and transmission of boundary harmonics are discussed. The solution of the nonlinear plane parallel slab is presented which describes the harmonic generation in experimental situations. An integral equation formulation for wave propagation in nonlinear media is sketched. Implications of the nonlinear boundary theory for experimental systems and devices are pointed out.

I. INTRODUCTION

THE high power densities available in light beams from coherent sources (lasers) have made possible the experimental observation of nonlinear effects, such as the doubling and tripling of the light frequency of one laser beam and mixing of frequencies between two laser beams.[1–5] The nonlinear properties of matter have been incorporated into Maxwell's equations and the solutions for the infinite nonlinear medium have been discussed in a recent paper.[6] The effects at the boundary of a nonlinear medium are the subject of the present paper. The use of the well-known boundary conditions for the macroscopic field quantities, which must now include the nonlinear polarization, leads to a generalization of the ancient laws of reflection and refraction of light. The law of the equality of the angles of incidence and reflection of light from a mirror was known in Greek antiquity and precisely formulated by Hero of Alexandria.[7] Snell's law for refraction[8] dates from 1621. Generalizations for the directions of light harmonic waves and waves at the sum or difference frequencies, if two light beams are incident on the boundary of a nonlinear medium, are given in Sec. III of this paper. The solution of Maxwell's equations with the proper boundary conditions leads to harmonic waves both in reflection and transmission.

The intensity and polarization conditions of the boundary harmonics are derived in Sec. IV. These results can be regarded as a generalization of Fresnel's laws,[8] which were derived on the basis of an elastic theory of light in 1823 for the linear case. There is an equivalent of Brewster's angle, at which the intensity of the reflected harmonic wave vanishes, if the E vector lies in the plane of the normal and reflected wave vector.

The nonlinear counterparts of the case of total reflection from a linear dielectric are discussed in Sec. V. The variety of nonlinear phenomena involving evanescent (exponentially decaying) waves is much wider than in the linear case. It will be shown that a totally reflected wave at the fundamental frequency may create both reflected and transmitted harmonic waves. Two normally refracted incident waves may give rise to evanescent waves at the difference frequency.

The plane parallel nonlinear slab is treated in Sec. VI. Expressions are given for the harmonic waves that emerge from both sides of the slab. There is a fundamental asymmetry between the cases in which the light waves approach the boundary from the linear or the nonlinear side. This asymmetry does not occur in the familiar linear case. In Sec. VII an integral equation formulation of light propagation in nonlinear media is sketched.

The results of this paper are discussed in the conclusion, Sec. VIII. The theoretical results have a direct bearing on experiments reported to date. In particular, the solutions presented here show in detail how the harmonic wave commences to grow when a fundamental wave enters a nonlinear crystal. Before the general solutions in more complicated situations are discussed, a simple example will be given in Sec. II to illustrate the basic physical phenomena at the nonlinear boundary.

II. HARMONIC WAVES EMANATING FROM A BOUNDARY: AN EXAMPLE

An example that contains all essential physical features is provided by the creation of second harmonic waves when a monochromatic plane wave at frequency ω_1 is incident on a plane boundary of a crystal which

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[6] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962). This paper will henceforth be referred to as ABDP.
[7] Hero of Alexandria, Κατοπτικα, 1st or 2nd Century A.D. Latin and German translation in Collected Papers (B. G. Teubner, Leipzig, 1899), Vol. 2. For a comprehensive historical account, see, for example, E. T. Whittaker, *A History of the Theories of the Aether and Electricity* (Nelson and Sons, London and Edinburgh, 1952), Vol. I.
[8] The well-known optical theory of reflection and refraction is treated in most textbooks of optics. See, for example, M. Born and E. Wolf, *Principles of Optics* (Pergamon Press, New York, 1959), Chaps. I and II.

lacks inversion symmetry. The light wave will be refracted into the crystal in the usual manner. In general, there will be two refracted rays in birefringent crystals. To avoid unnecessary complications, only one refracted ray will be assumed. This would be true experimentally in a cubic crystal such as ZnS, or for a uniaxial crystal, such as potassium dihydrogen phosphate (KDP), when the plane of incidence contains the optic axis and the incident light wave is, e.g., polarized within this plane. Choose the coordinate system such that the boundary is given by $z=0$, and the plane of incidence by $y=0$. The wave vector of the incident wave is $\mathbf{k}_1{}^i$ and of the refracted ray, $\mathbf{k}_1{}^T$. The latter is determined by Snell's law. The amplitude of the refracted ray, $\mathbf{E}_1{}^T$ is determined by Fresnel's laws for the linear medium.

The nonlinear susceptibility of the medium will give rise to a polarization at the harmonic frequencies, which in turn will radiate energy at these frequencies. The effective nonlinear source term at the second harmonic frequency $\omega_2=2\omega_1$ is given by

$$\begin{aligned}\hat{p}P^{\mathrm{NLS}}&=\mathbf{P}^{\mathrm{NLS}}(2\omega_1)\\&=\chi(\omega_2=2\omega_1):\mathbf{E}_1{}^T\mathbf{E}_1{}^T\exp i(\mathbf{k}^S\cdot\mathbf{r}-2\omega_1 t).\end{aligned}\tag{2.1}$$

The wave vector of the source term is twice the wave vector of the refracted fundamental ray, $\mathbf{k}^S=2\mathbf{k}_1{}^T$. The nonlinear source was introduced by ABDP,[6] who showed how the susceptibility tensor can be related to the nonlinear atomic properties of the medium. They also showed that the effective nonlinear source term can readily be incorporated into Maxwell's equations for the nonlinear medium,

$$\nabla\times\mathbf{E}=-\frac{1}{c}\frac{\partial\boldsymbol{\mu}\mathbf{H}}{\partial t},\tag{2.2}$$

$$\nabla\times\mathbf{H}=\frac{1}{c}\frac{\partial(\boldsymbol{\varepsilon}\mathbf{E})}{\partial t}+\frac{4\pi}{c}\frac{\partial\mathbf{P}^{\mathrm{NLS}}}{\partial t}.\tag{2.3}$$

Consistent with the assumption of a cubic crystal or a special geometry, ϵ will be taken as a scalar and $\mu=1$. Waves at the second harmonic frequency will obey the wave equation

$$\nabla\times\nabla\times\mathbf{E}_2+\frac{\boldsymbol{\varepsilon}(2\omega_1)}{c}\frac{\partial^2\mathbf{E}_2}{\partial t^2}=-\frac{4\pi}{c^2}\frac{\partial^2\mathbf{P}^{\mathrm{NLS}}(2\omega_1)}{\partial t^2}.\tag{2.4}$$

It is important to note that this is the usual linear wave equation augmented by a source term on the right-hand side. The general solution consists of the solution of the homogeneous equation plus one particular solution of the inhomogeneous equation,

$$\begin{aligned}\mathbf{E}_2{}^T&=\hat{e}_T\mathcal{E}_2{}^T\exp i(\mathbf{k}_2{}^T\cdot\mathbf{r}-2\omega_1 t)-\frac{4\pi P_2{}^{\mathrm{NLS}}(4\omega_1{}^2/c^2)}{(k_2{}^T)^2-(k^S)^2}\\&\quad\times\left[\hat{p}-\frac{\mathbf{k}^S(\mathbf{k}^S\cdot\hat{p})}{(k^T)^2}\right]\exp i(\mathbf{k}^S\cdot\mathbf{r}-2\omega_1 t),\\\mathbf{H}_2{}^T&=\frac{c}{2\omega_1}(\mathbf{k}_2{}^T\times\hat{e}_T)\mathcal{E}_2{}^T\exp i(\mathbf{k}_2{}^T\cdot\mathbf{r}-2\omega_1 t)\\&\quad-\frac{4\pi P^{\mathrm{NLS}}(4\omega_1{}^2/c^2)}{(k_2{}^T)^2-(k^S)^2}\frac{c}{2\omega_1}(\mathbf{k}^S\times\hat{p})\exp i(\mathbf{k}^S\cdot\mathbf{r}-2\omega_1 t).\end{aligned}\tag{2.5}$$

In vacuum the usual plane wave solutions of the homogeneous wave equation are

$$\begin{aligned}\mathbf{E}_2{}^R&=\hat{e}_R\mathcal{E}_2{}^R\exp(i\mathbf{k}_2{}^R\cdot\mathbf{r}-2i\omega_1 t),\\\mathbf{H}_2{}^R&=(c/2\omega_1)(\mathbf{k}_2{}^R\times\hat{e}_R)\mathcal{E}_2{}^R\exp(i\mathbf{k}_2{}^R\cdot\mathbf{r}-2i\omega_1 t).\end{aligned}\tag{2.6}$$

The direction of the wave vectors of the reflected wave $\mathbf{k}_2{}^R$ and the homogeneous transmitted wave(s) $\mathbf{k}_2{}^T$, as well as the polarization vectors $\hat{e}_T$ and $\hat{e}_R$ and the magnitude of the reflected and transmitted amplitudes $\mathcal{E}_2{}^R$ and $\mathcal{E}_2{}^T$ have to be determined from the boundary conditions. It turns out that the nonlinear polarization radiates in one particular direction back into vacuum, and in one direction into the medium (or, in the general anisotropic case, in two directions). The problem is very similar to the problem of linear reflection and refraction, except for the fact that the role of the incident wave has been taken over by the "inhomogeneous wave" with an amplitude proportional to P^{NLS}.

The tangential components of $\mathbf{E}$ and $\mathbf{H}$ should be continuous everywhere on the boundary at all times. This requires that the individual frequency components, at ω_1 and $2\omega_1$, are separately continuous across the boundary. To satisfy this condition for all points on the boundary simultaneously, one requires for the fundamental frequency

$$k_{1x}{}^i=k_{1x}{}^R=k_{1x}{}^T.$$

The tangential dependence of the wave at $2\omega_1$ is determined by P^{NLS}:

$$2k_{1x}{}^T=k_{2x}{}^S=k_{2x}{}^R=k_{2x}{}^T.$$

These relations reflect the general requirement of conservation of the tangential component of momentum. With our choice of coordinate system, all y components of the wave vectors are zero. Since the absolute values of the wave vectors are determined by the dielectric constant, $|k_2{}^T|=[\epsilon(2\omega)]^{1/2}(2\omega/c)$, etc., the angles of reflection and refraction of the second harmonic follow immediately,

$$\begin{aligned}&\sin\theta_2{}^R=k_{2x}{}^R/|k_2{}^R|=k_{1x}{}^i/|k_1{}^R|=\sin\theta^i,\\&\sin\theta_2{}^T=k_{2x}{}^T/|k_2{}^T|=\epsilon^{-1/2}(2\omega)\sin\theta^i,\\&\sin\theta^S=\epsilon^{-1/2}(\omega)\sin\theta^i.\end{aligned}\tag{2.7}$$

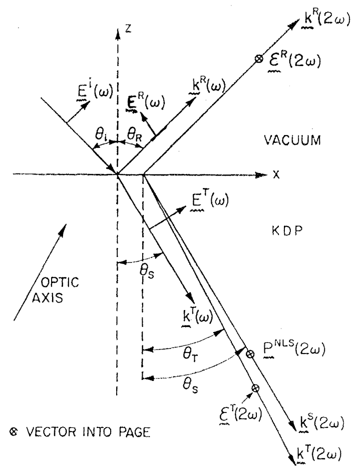

FIG. 1. The incident, reflected, and refracted rays at the fundamental and second harmonic frequencies near the boundary between a KDP crystal and vacuum. There is no matching of the phase velocities between the extraordinary fundamental and ordinary second harmonic ray.

Since the vacuum has no dispersion, the reflected second harmonic goes in the same direction as the reflected fundamental wave. Whereas the inhomogeneous source wave goes in the same direction as the transmitted fundamental, the homogeneous transmitted harmonic will in general go in a somewhat different direction. The two waves will be parallel in the limiting case of exact phase matching, $\epsilon(\omega)=\epsilon(2\omega)$, or normal incidence. The solution of the wave equation, Eq. (2.4), requires further scrutiny in this limiting case. This will be postponed to Sec. IV. The important question of mismatch of the phase velocities in the direction normal to the propagation had to remain unsolved in the discussion of the infinite medium.[6] It has now been resolved; this mismatch is determined both by the orientation of the boundary and the dispersion in the medium. The geometrical relationships are sketched in Fig. 1.

The question of the intensity and polarization of the harmonic waves will be treated here only for the case that the nonlinear polarization is normal to the plane of incidence, i.e., $\hat{p}=\hat{y}$. A more general discussion will be postponed until Sec. IV. The example considered here occurs in a KDP crystal when the fundamental incident wave is E polarized in the plane of incidence, which is the optic (c) axis of the crystal. This is shown by considering the symmetry of χ. If the transmitted fundamental wave is the extraordinary ray, the field E_1^T will, in general, have x' and z' components. The coordinate system (x',y',z') is fixed with respect to the crystal. The z' direction coincides with the optic axis and y' coincides with y. Since the only nonvanishing elements in the nonlinear tensor susceptibility are $\chi_{x'y'z'}$, the nonlinear source term will be polarized in $y'=y$ direction according to Eq. (2.1).

The boundary conditions, which match the wave solutions in Eqs. (2.5) and (2.6), can now be satisfied by choosing harmonic waves with an electric field vector normal to the plane of incidence, $\hat{e}_T=\hat{e}_R=\hat{y}$. These are the ordinary rays in the geometry of Fig. 1. The continuity of the tangential components E_y at the boundary $z=0$ leads to the condition

$$\mathcal{E}_2{}^R=\mathcal{E}_2{}^T-4\pi P^{\mathrm{NLS}}/[\epsilon(2\omega)-\epsilon(\omega)]. \tag{2.8}$$

The continuity of the x components of the magnetic field requires

$$-\mathcal{E}_2{}^R\cos\theta^R=\epsilon^{1/2}(2\omega)\,\mathcal{E}_2{}^T\cos\theta^T-\epsilon^{1/2}(\omega)\cos\theta^S\frac{4\pi P^{\mathrm{NLS}}}{\epsilon(2\omega)-\epsilon(\omega)}. \tag{2.9}$$

The electric field amplitudes of the reflected and transmitted harmonic follow from the solution of Eqs. (2.8) and (2.9).

$$\mathcal{E}_2{}^R=\frac{-4\pi P^{\mathrm{NLS}}}{\epsilon(2\omega)-\epsilon(\omega)}\,\frac{\epsilon^{1/2}(2\omega)\cos\theta^T-\epsilon^{1/2}(\omega)\cos\theta^S}{\epsilon^{1/2}(2\omega)\cos\theta^T+\cos\theta^R}. \tag{2.10}$$

$\mathcal{E}_2{}^T$ follows immediately from Eq. (2.8). It should be kept in mind that the total field in the dielectric medium is, of course, given by the interference between the homogeneous and the inhomogeneous wave [according to Eq. (2.5)]. At the boundary the total field in the medium is of course equal to $\mathcal{E}^R$. Multiplication of both numerator and denominator of Eq. (2.10) by $\epsilon^{1/2}(2\omega)\cos\theta^T+\epsilon^{1/2}(\omega)\cos\theta^S$, and use of the refraction laws [Eq. (2.7)] lead to

$$\mathcal{E}_2{}^R=\frac{-4\pi P^{\mathrm{NLS}}}{[\epsilon^{1/2}(2\omega)\cos\theta^T+\cos\theta^R][\epsilon^{1/2}(2\omega)\cos\theta^T+\epsilon^{1/2}(\omega)\cos\theta^S]}, \tag{2.11a}$$

or

$$\mathcal{E}_2{}^R=\frac{-4\pi P^{\mathrm{NLS}}\sin^2\theta^T\sin\theta^S}{\sin(\theta^i+\theta^T)\sin(\theta^T+\theta^S)\sin\theta^i}. \tag{2.11b}$$

The amplitude of the reflected wave is not sensitive to matching of the phase velocities in the medium. In fact, the ordinary harmonic and the extraordinary fundamental cannot be matched in KDP. Crudely, one may say that a layer of about one wavelength thick contributes to the radiation of the reflected ray. Deeper strata of the semi-infinite medium interfere destructively and together give no contribution to the reflected ray. This statement will be made more precise in Sec. VI, where a dielectric slab of finite thickness will be considered explicitly. If $E_{\mathrm{at}}\sim3\times10^8$ V/cm denotes the typical intra-atomic field, the fraction of the incident power that will appear in the reflected harmonic is roughly $(E_1{}^T/E_{\mathrm{at}})^2$. For a relatively modest flux density of 10^5 W/cm^2 this is about 4×10^{-10}. Since harmonic power conversion ratios of less than $1:10^{12}$ have been detected, the reflected harmonic should be readily observable. Peak powers of 10^7 W/cm^2 in unfocused laser beams have been obtained.

Any attempt to calculate the angular dependence of the reflected harmonic from Eqs. (2.11a) and (2.11b) should take proper account of the variation of P^{NLS} itself with angle. The Fresnel equations for linear media cause the fundamental waves to have certain angular dependence and this is passed on to P^{NLS}.

The transmitted wave starts with an intensity of about the same magnitude. However, this wave will grow, because the destructive interference between the homogeneous and inhomogeneous solutions diminishes as one moves away from the boundary. A detailed analysis will again be postponed till Sec. IV, where this wave will be matched to the solutions obtained previously for the infinite medium.

The total power flow is, of course, conserved because the fundamental wave will have reflected and transmitted intensities slightly less than in the case of a strictly linear dielectric. Formally, this would follow from the introduction of $P^{\mathrm{NLS}}(\omega_1)$ arising as the beat between the second harmonic wave with the fundamental itself. Since the fractional conversion at the boundary will always be small, it is justified to treat the fundamental intensity as a fixed constant parameter in deriving the harmonic waves. The depletion of the fundamental power in the body of the nonlinear dielectric has been discussed in detail by ABDP. That generalization of the parametric theory is, fortunately, not necessary in discussing boundary problems.

III. GENERAL LAWS OF REFLECTION AND REFRACTION

Consider a boundary ($z=0$) between a linear medium, with incident and reflected waves characterized by labels "i" and "R," respectively, and a nonlinear medium with the transmitted waves, labeled "T." Two incident plane waves, $\mathbf{E}_1\exp(i\mathbf{k}_1{}^i\cdot\mathbf{r}-i\omega_1 t)$ and $\mathbf{E}_2\exp(i\mathbf{k}_2{}^i\cdot\mathbf{r}-i\omega_2 t)$, approach the boundary from the side of the linear medium.

In general, waves at all sum and differencies $m_1\omega_1 \pm m_2\omega_2$ will emanate from the boundary (m_1 and m_2 are integers). The sum frequency $\omega_3=\omega_1+\omega_2$ will be considered explicitly. The extension of the procedure to the difference frequency $\omega_1-\omega_2$, other harmonic combinations, and to the situation when three or more waves are incident, will be obvious.

The geometry is defined in Fig. 2. The angles of incidence of the two waves are $\theta_1{}^i$ and $\theta_2{}^i$, the planes of incidence make an angle ϕ with each other. Choose the x and y direction of the coordinate system such that $k_{1y}{}^i=-k_{2y}{}^i$.

A necessary and sufficient condition for the requirement that the boundary conditions will be satisfied

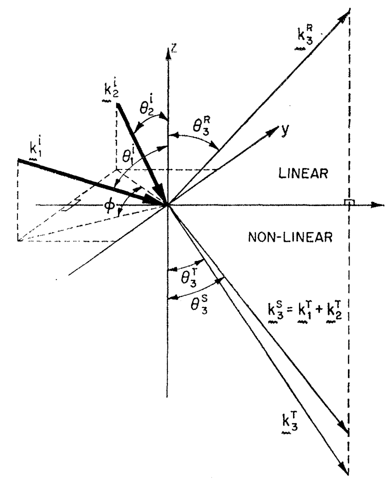

FIG. 2. Two incident rays at frequencies ω_1 and ω_2 create a reflected wave, a homogeneous and an inhomogeneous transmitted wave at the sum frequency $\omega_3=\omega_1+\omega_2$, all emanating from the boundary between the linear and nonlinear medium.

simultaneously at all points in the plane $z=0$ is that the x and y components of the momentum wave vector remain conserved. For the sum wave, this leads to the conditions,

$$\begin{aligned}k_{3x}{}^R&=k_{3x}{}^T=k_{3x}{}^S=k_{1x}{}^T+k_{2x}{}^T=k_{1x}{}^i+k_{2x}{}^i,\\ k_{3y}{}^R&=k_{3y}{}^T=k_{3y}{}^S=k_{1y}{}^T+k_{2y}{}^T=k_{1y}{}^i+k_{2y}{}^i=0.\end{aligned}\tag{3.1}$$

This leads immediately to the following theorem. The inhomogeneous source wave, the homogeneous transmitted and reflected waves at the sum frequency and the boundary normal all lie in the same plane. With our choice of coordinate system this "plane of sum reflection" is the xz plane. A similar theorem holds for the difference frequency and other harmonic waves, although their planes of reflection will in general all be different.

The propagation of the inhomogeneous wave at the sum frequency, proportional to $P^{\mathrm{NLS}}(\omega_3)$, is given by $\exp\{i(\mathbf{k}_1{}^T+\mathbf{k}_2{}^T)\cdot\mathbf{r}-i(\omega_1+\omega_2)t\}$. Its angle with the normal into the nonlinear medium $\theta_3{}^S$ is determined by

$$\sin\theta_3{}^S=|k_{1x}{}^T+k_{2x}{}^T|/|\mathbf{k}_1{}^T+\mathbf{k}_2{}^T|.$$

The wave vectors $\mathbf{k}_1{}^T$ and $\mathbf{k}_2{}^T$ are given by Snell's law for refraction in the usual linear case. The convention is made that all angles with the normal are defined in the interval 0 to $\pi/2$. The angle ϕ between the planes of incidence goes from 0 to π. From simple trigonometric relationships, one finds

$$\begin{aligned}|k_3{}^T|^2\sin^2\theta_3{}^T&=|k_3{}^R|^2\sin^2\theta_3{}^R\\&=|k_1{}^i|^2\sin^2\theta_1{}^i+|k_2{}^i|^2\sin^2\theta_2{}^i\\&\quad+2|k_1{}^i|\,|k_2{}^i|\sin\theta_1{}^i\sin\theta_2{}^i\cos\phi.\end{aligned}\tag{3.2}$$

If the dielectric constants are introduced by means of the relationship, $\epsilon=k^2(\omega^2/c^2)^{-1}$, Eq. (3.2) can be rewritten as

$$\begin{aligned}\epsilon_3{}^T\omega_3{}^2\sin^2\theta_3{}^T&=\epsilon_3{}^R\omega_3{}^2\sin^2\theta_3{}^R\\&=\epsilon_1{}^R\omega_1{}^2\sin^2\theta_1{}^i+\epsilon_2{}^R\omega_2{}^2\sin^2\theta_2{}^i\\&\quad+2(\epsilon_1{}^R\epsilon_2{}^R)^{1/2}\omega_1\omega_2\sin\theta_1{}^i\sin\theta_2{}^i\cos\phi.\end{aligned}\tag{3.3}$$

Superscripts R and T refer to the linear and nonlinear medium, respectively, subscripts refer to the frequencies. It is advantageous to introduce an effective dielectric constant ϵ^S for the nonlinear source wave, defined by

$$\epsilon^S \sin^2\theta_3{}^S=\epsilon_3{}^T \sin^2\theta_3{}^T=\epsilon_3{}^R \sin^2\theta_3{}^R. \tag{3.4}$$

In the special case that the planes of incidence coincide, a simple relationship is obtained which shows a striking resemblance to Snell's law:

$$(\epsilon_3{}^T)^{1/2} \sin\theta_3{}^T=(\omega_1/\omega_3)(\epsilon_1{}^R)^{1/2} \sin\theta_1{}^i \pm(\omega_2/\omega_3)(\epsilon_2{}^R)^{1/2} \sin\theta_2{}^i. \tag{3.5}$$

The + sign is to be used if the two incident rays are on the same side of the normal, the − sign if they are on opposite sides. If the linear medium is optically denser than the nonlinear medium, $\epsilon_1{}^R\sim\epsilon_2{}^R>\epsilon_3{}^T$, the possibility exists that $\sin\theta_3{}^T>1$. This case of total reflection will be discussed in detail in Sec. V, after the question of intensity and polarization has been taken up. If one considers the difference frequency $\omega_{-3}=\omega_1-\omega_2$, the counterparts of Eqs. (3.1)–(3.3) can readily be written down. For the sake of brevity, only the analog of Eq. (3.5) will be reproduced;

$$(\epsilon_{-3}{}^R)^{1/2} \sin\theta_{-3}{}^R=(\epsilon_{-3}{}^T)^{1/2} \sin\theta_{-3}{}^T =(\omega_1/\omega_{-3})(\epsilon_1{}^R)^{1/2} \sin\theta_1{}^i\mp(\omega_2/\omega_{-3})(\epsilon_2{}^R)^{1/2} \sin\theta_2{}^i. \tag{3.6}$$

The + sign must now be used if the incident waves approach from opposite sides of the normal. Since $\omega_1/\omega_{-3}>1$, there is now ample opportunity for the case $\sin\theta_{-3}{}^R>1$. There will be no reflected power at the difference frequency. This situation has no counterpart in the linear theory. When $\epsilon_{-3}{}^T>\epsilon_{-3}{}^R$, even if $\sin\theta_{-3}{}^R>1$, there still exist the two possibilities, $\sin\theta_{-3}{}^T>1$ or <1. The problems of total reflection and transmission are clearly more varied in the nonlinear case and will be discussed in Sec. V.

The example of second harmonic generation of the previous section follows from Eq. (3.3) if one puts $\theta_1{}^i=\theta_2{}^i$ and $\phi=0$, and $\epsilon_1{}^R=\epsilon_2{}^R=\epsilon_3{}^R$. In general, the sum and difference frequencies will be reflected in the same direction as ω_1 and ω_2, if the incident rays come from the same direction in a dispersionless medium.

The conditions of conservation of the tangential component of momentum, [Eq. (3.1)], are general. They can easily be used to derive the directional relationships for higher harmonics. They hold regardless of whether the harmonic radiation is of dipolar, electric or magnetic, or quadrupolar origin. They also hold for anisotropic media. In this case, there are usually two directions of the wave vector with a given tangential component. There will be, in general, four inhomogeneous waves at the sum frequency, corresponding to mixing of two refracted waves at ω_1 with two refracted waves at ω_2. There will be two homogeneous transmitted waves $\theta_3{}^T$, and two reflected directions $\theta_3{}^R$, if the linear medium is also anisotropic.

IV. POLARIZATION AND INTENSITIES OF THE HARMONIC WAVES

In this section the discussion will be restricted to isotropic materials, although the example of Sec. II showed that the discussion is also immediately applicable to special geometries with anisotropic crystals. There are no fundamental difficulties in extending the calculations to the general anisotropic case, but the resulting algebraic complexity does not make such an effort worthwhile at the present time.

The starting point for the calculation of the polarization and the intensity of the waves at the sum frequency $\omega_3=\omega_1+\omega_2$ is the nonlinear polarization induced in the medium,

$$\mathbf{P}^{\mathrm{NLS}}(\omega_3)=\chi(\omega_3=\omega_1+\omega_2):\mathbf{E}_1{}^T\mathbf{E}_2{}^T \times\exp i[(\mathbf{k}_1{}^T+\mathbf{k}_2{}^T)\cdot\mathbf{r}-\omega_3 t]. \tag{4.1}$$

The refracted waves at ω_1 and ω_2 are known in terms of the incident waves by means of the formulas of Snell and Fresnel for the incident medium. Therefore, the nonlinear source at ω_3 is known. The angular dependence of P^{NLS} itself is derived from the transmitted linear waves given by the usual Fresnel equations. One must take proper account of this in analyzing the directional dependence of harmonic generation. As in the linear case, waves at ω_3 with the electric field vector normal to the plane of reflection ($E_\perp$), defined in the preceding section, can be treated independently from waves with the electric field vector in the plane of reflection ($E_{\parallel}$).

A. Perpendicular Polarization, $E_y=E_\perp$, $E_x=E_z=0$

This wave is created by $P_y{}^{\mathrm{NLS}}=P_\perp{}^{\mathrm{NLS}}$. The continuity of the tangential components of the solutions Eq. (2.5) and Eq. (2.6) at the boundary requires in this case, shown in Fig. 3,

$$E_y=E_\perp{}^R=\mathcal{E}_\perp{}^T+4\pi P_\perp{}^{\mathrm{NLS}}(\epsilon_S-\epsilon_T)^{-1}, \tag{4.2}$$

$$H_x=-\epsilon_R{}^{1/2}E_\perp{}^R \cos\theta_R=\epsilon_T{}^{1/2}\mathcal{E}_\perp{}^T \cos\theta_T +4\pi\epsilon_S{}^{1/2}(\epsilon_S-\epsilon_T)^{-1}P_\perp{}^{\mathrm{NLS}} \cos\theta_S. \tag{4.3}$$

The continuity of the normal components of **D** and **B** follows automatically from the conditions [Eqs. (4.2) and (4.3)] and the law of refraction [Eq. (3.3)]. The subscript 3 has been suppressed, since all waves and source terms refer to the frequency ω_3. Henceforth R, S, and T will be written as subscripts rather than superscripts, as in Eq. (4.3), for neater appearance.

The solution of Eqs. (4.2) and (4.3) gives

$$E_\perp{}^R=-\frac{4\pi P_\perp{}^{\mathrm{NLS}}}{\epsilon_T-\epsilon_S}\left[\frac{\epsilon_T{}^{1/2} \cos\theta_T-\epsilon_S{}^{1/2} \cos\theta_S}{\epsilon_T{}^{1/2} \cos\theta_T+\epsilon_R{}^{1/2} \cos\theta_R}\right]. \tag{4.4}$$

After some manipulation which was already described in Sec. II, the reflected sum wave amplitude may be

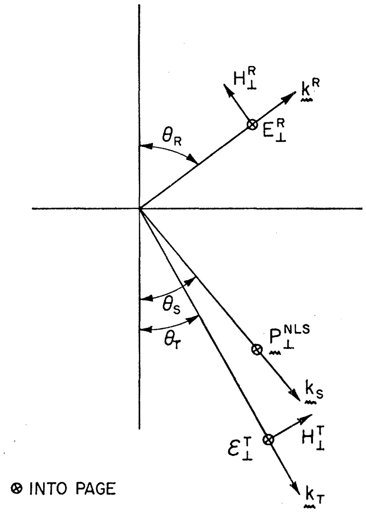

FIG. 3. The harmonic waves at the boundary of a nonlinear medium, polarized with the electric field vector normal to the plane of reflection.

written as

$$E_\perp{}^R=-4\pi P_\perp{}^{\mathrm{NLS}}[(\epsilon_T{}^{1/2}\cos\theta_T+\epsilon_R{}^{1/2}\cos\theta_R)\times(\epsilon_T{}^{1/2}\cos\theta_T+\epsilon_S{}^{1/2}\cos\theta_S)]^{-1}$$
$$=-4\pi P_\perp{}^{\mathrm{NLS}}\sin^2\theta_T\sin\theta_S[\sin(\theta_R+\theta_T)\times\sin(\theta_S+\theta_T)\sin\theta_R]^{-1}. \quad (4.5)$$

The amplitude is 180° out of phase with the nonlinear polarization.

The transmitted wave is given by

$$E_\perp{}^T=-\frac{4\pi P_\perp{}^{\mathrm{NLS}}}{\epsilon_T-\epsilon_S}\left[\exp(i\mathbf{k}^S\cdot\mathbf{r}-i\omega_3 t)-\frac{\epsilon_S{}^{1/2}\cos\theta_S+\epsilon_R{}^{1/2}\cos\theta_R}{\epsilon_T{}^{1/2}\cos\theta_T+\epsilon_R{}^{1/2}\cos\theta_R}\exp(i\mathbf{k}^T\cdot\mathbf{r}-i\omega_3 t)\right]. \quad (4.6)$$

Since

$$\mathbf{k}^S-\mathbf{k}^T=\omega c^{-1}[(\epsilon_S)^{1/2}\cos\theta_S-(\epsilon_T)^{1/2}\cos\theta_T]\hat{z}, \quad (4.7)$$

Eq. (4.6) can be transformed to a single plane wave with a propagation vector $\mathbf{k}^T$, but with an amplitude

$$E_\perp{}^T=E_\perp{}^R+4\pi P^{\mathrm{NLS}}\times\frac{\exp[\omega c^{-1}(\epsilon_S{}^{1/2}\cos\theta_S-\epsilon_T{}^{1/2}\cos\theta_T)z]-1}{\epsilon_S-\epsilon_T} \quad (4.8)$$

varying with the distance z from the boundary.

For values of z which satisfy the condition

$$\omega c^{-1}z(\epsilon_S{}^{1/2}\cos\theta_S-\epsilon_T{}^{1/2}\cos\theta_T)\ll 1, \quad (4.7a)$$

the amplitude of the transmitted wave behaves as

$$E_\perp{}^T=E_\perp{}^R+4\pi iP^{\mathrm{NLS}}(\omega c^{-1}z)\times(\epsilon_S{}^{1/2}\cos\theta_S+\epsilon_T{}^{1/2}\cos\theta_T)^{-1}. \quad (4.8a)$$

The wave starts off with a value $E_\perp{}^R$ given by Eq. (4.5), but a 90° out-of-phase component starts growing proportional to the distance z from the boundary. This is precisely the effect of harmonic generation in the volume of an infinite medium, discussed in ABDP. For an appreciable phase mismatch, the condition [Eq. (4.7a)] will be violated after some distance which may be called the coherence length. Equation (4.6) shows that the intensity of the transmitted wave will then vary sinusoidally with the distance from the boundary. In the case of perfect matching, Eq. (4.8a) would indicate that the intensity increases proportional to the square of the distance, beyond all limits. Actually, the parametric approach breaks down in this case, and the reaction of the harmonic wave on the incident intensities should be taken into account. It is straightforward to match the solutions of ABDP so that they give the proper expansion [Eq. (4.8a)] for small z. This expression shows how the harmonic wave starts at the boundary and gives the proper initial conditions to be used for the coupled amplitude equations in ABDP. The amplitudes at ω_1 and ω_2 initially have a constant value and decrease only proportional to z^2.

It should be noted that the transmitted wave is an inhomogeneous plane wave, since the amplitude is not constant in a plane of constant phase. An exception to this occurs when the waves propagate normal to the boundary. In this special case the amplitudes of the reflected and transmitted waves are given by

$$E_n{}^R=-4\pi P_\perp{}^{\mathrm{NLS}}(\epsilon_T{}^{1/2}+\epsilon_R{}^{1/2})^{-1}(\epsilon_T{}^{1/2}+\epsilon_S{}^{1/2})^{-1},$$
$$E_n{}^T=E_n{}^R+4\pi P_\perp{}^{\mathrm{NLS}}\times\frac{[\exp(i(\epsilon_S{}^{1/2}-\epsilon_T{}^{1/2})\omega c^{-1}z)-1]}{\epsilon_S-\epsilon_T}. \quad (4.9)$$

The transmitted wave varies both in amplitude and phase as the wave progresses into the nonlinear medium.

B. Parallel Polarization, $E_y=P_y{}^{\mathrm{NLS}}=0$

These harmonic waves are created by the x and z components of the nonlinear polarization. It will be advantageous to describe the nonlinear polarization in the plane of reflection by its magnitude $P_{\parallel}{}^{\mathrm{NLS}}$ and the angle α between its direction and the direction of propagation of the source $\mathbf{k}^S$. The continuity of the tangential components at $z=0$ now requires, as will be evident from Eqs. (2.5) and (2.6) and Fig. 4,

$$E_x=-E_{\parallel}{}^R\cos\theta_R=\mathcal{E}_{\parallel}{}^T\cos\theta_T+\frac{4\pi P_{\parallel}{}^{\mathrm{NLS}}\sin\alpha\cos\theta_S}{\epsilon_S-\epsilon_T}-\frac{4\pi P_{\parallel}\cos\alpha\sin\theta_S}{\epsilon_T}, \quad (4.10)$$

$$H_y=-\epsilon_R{}^{1/2}E^R=-\epsilon_T{}^{1/2}\mathcal{E}_{\parallel}{}^T-\epsilon_S{}^{1/2}\frac{4\pi P_{\parallel}{}^{\mathrm{NLS}}\sin\alpha}{\epsilon_S-\epsilon_T}. \quad (4.11)$$

The last term in Eq. (4.10) arises from the longitudinal component of $\mathbf{E}$. There is, of course, no longitudinal component of $\mathbf{D}$ or $\mathbf{H}$. The continuity of the normal

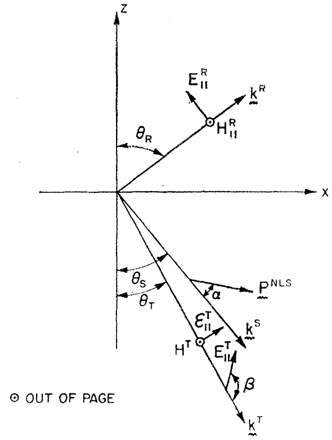

FIG. 4. The harmonic wave at the boundary of a nonlinear medium, with the electric field vector in the plane of reflection. Both the nonlinear polarization and the electric field may have longitudinal components.

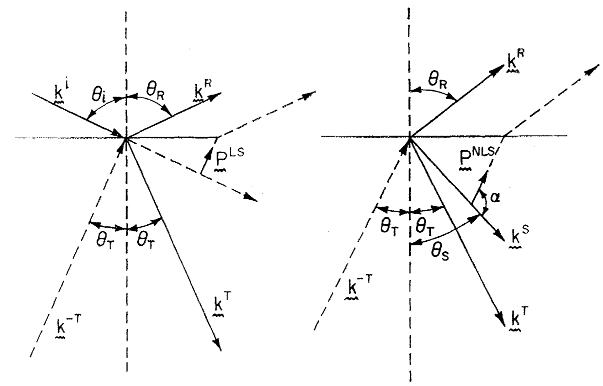

FIG. 5. Brewster angle for linear and nonlinear reflection. The *total* polarization cannot radiate in the direction of the reflected ray in *vacuum*. The *source* polarization cannot radiate into the direction $\mathbf{k}_{-T}$ in the *medium*, which would lead to a reflected ray in vacuum.

components of these quantities at the boundary is automatically satisfied by Eqs. (3.3), (4.10), and (4.11). Elimination of $\mathcal{E}_{\parallel}{}^T$ between the last two equations yields the amplitude of the reflected wave

$$E_{\parallel}{}^R=\frac{4\pi P_{\parallel}{}^{\mathrm{NLS}}\sin\alpha}{\epsilon_R{}^{1/2}\cos\theta_T+\epsilon_T{}^{1/2}\cos\theta_R}\times\frac{1-(\epsilon_S{}^{-1}+\epsilon_T{}^{-1})\epsilon_R\sin^2\theta_R}{\epsilon_S{}^{1/2}\cos\theta_T+\epsilon_T{}^{1/2}\cos\theta_S}+\frac{4\pi P_{\parallel}{}^{\mathrm{NLS}}\cos\alpha\sin\theta_S}{\epsilon_T{}^{1/2}\epsilon_S{}^{1/2}\cos\theta_T+\epsilon_T\cos\theta_R}. \quad (4.12)$$

This expression can be transformed by further use of Eq. (3.3) into

$$E_{\parallel}{}^R=\frac{4\pi P_{\parallel}{}^{\mathrm{NLS}}\sin\theta_S\sin^2\theta_T\sin(\alpha+\theta_T+\theta_S)}{\epsilon_R\sin\theta_R\sin(\theta_T+\theta_S)\sin(\theta_T+\theta_R)\cos(\theta_T-\theta_R)}. \quad (4.13)$$

There is no anomaly in the reflected intensity when the condition of phase velocity matching $\theta_S=\theta_T$ is approached. In the limit of normal reflection, $\theta_S=\theta_T=\theta_R=0$, Eq. (4.12) takes on the same form as Eq. (4.9), except for a minus sign. This difference is trivial and a consequence of the conventions made in Figs. 3 and 4. In the case of normal reflection there is no distinction between parallel and perpendicular polarization.

Equation (4.13) reveals the existence of a Brewster angle for harmonic waves, when $E_{\parallel}{}^R=0$. For $\theta_T=\pi-\alpha-\theta_S$, the reflected harmonic is completely polarized normal to the plane of reflection. This condition implies that the nonlinear polarization is parallel to that direction of propagation in the nonlinear medium, which on refraction into the linear medium gives rise to the reflected ray in the direction θ_R. The physical interpretation of Brewster's angle is thus that the nonlinear polarization cannot radiate *inside* the medium in the direction which would otherwise yield a reflected ray. This interpretation appears at first sight to conflict with the simple explanation of Brewster's angle in the linear case. There one says that the polarization cannot radiate in *vacuum* parallel to its own direction, which leads to $\theta_R+\theta_T=\pi/2$.

It is shown in Fig. 5 that the two interpretations can be reconciled. One may consider the polarization induced by the incident *vacuum* wave as the linear source, P^{LS}. This source radiates *inside the medium.* This takes care of the dipolar interaction in the lattice and this is the way in which we have viewed the nonlinear polarization. Conversely, we could have calculated the total polarization of the lattice at the sum frequency, including both the linear and nonlinear part. This total polarization should be considered to radiate in vacuum and this would lead to the usual interpretation of Brewster's angle, that the total polarization is parallel to the reflected direction. To sum up, the dipolar interaction or Lorentz field should be taken into account once, and this can either be done in the calculation of the total polarization, which then radiates into vacuum, or on the side of the radiation field in the *medium* created by a polarization induced by a wave in vacuum. The question raised here is purely semantic in nature. Maxwell's equations, of course, take correct account of the dipolar interactions in the material.

The transmitted wave with polarization in the plane of transmission can be obtained by substituting into Eq. (2.5) the values of $P_{\parallel}{}^{\mathrm{NLS}}$ and $\mathcal{E}_{\parallel}{}^T$. This last quantity is given by Eqs. (4.11) and (4.12). It is again possible, by means of Eq. (4.7), to write the transmitted wave as a single wave propagating in the direction $\mathbf{k}_T$, but with an amplitude that depends on the distance z from the boundary. The electric-field amplitude of the combined transmitted wave, $E_{\parallel}{}^T$, will, in general, have a longitudinal component, as well as a transverse component. With the introduction of the angle β between $E_{\parallel}{}^T$ and the direction of propagation $\mathbf{k}_T$, the transverse component of the total transmitted wave may, after some manipulation, be written as

$$E_{\|}^{T}\sin\beta=\frac{4\pi P_{\|}^{\mathrm{NLS}}\sin\theta_S\sin\theta_T\sin(\alpha+\theta_T+\theta_S)}{\epsilon_T\sin(\theta_T+\theta_S)\sin(\theta_T+\theta_R)\cos(\theta_T-\theta_R)}-\frac{4\pi P_{\|}^{\mathrm{NLS}}\sin\alpha\sin\theta_S\cos\theta_S}{\epsilon_T\sin(\theta_T+\theta_S)}$$
$$+4\pi P_{\|}^{\mathrm{NLS}}\cos\alpha\sin(\theta_T-\theta_S)\epsilon_T^{-1}\times\exp\{i\omega c^{-1}z(\epsilon_S^{1/2}\cos\theta_S-\epsilon_T^{1/2}\cos\theta_T)\}$$
$$+4\pi P_{\|}^{\mathrm{NLS}}\sin\alpha\cos(\theta_T-\theta_S)\times\frac{\exp\{i\omega c^{-1}z(\epsilon_S^{1/2}\cos\theta_S-\epsilon_T^{1/2}\cos\theta_T)\}-1}{\epsilon_S-\epsilon_T}. \quad (4.14)$$

The first three terms give the constant value with which this component starts at the boundary, the last term displays the variation with z due to the interference between the homogeneous and inhomogeneous solution. For values of z which are small enough so that no appreciable dephasing has occurred, the intensity of the wave increases proportional to z^2. The amplitude has a component, 90° out of phase in the time domain, given by

$$4\pi P_{\|}^{\mathrm{NLS}}\frac{\sin\alpha\cos(\theta_T-\theta_S)}{\epsilon_S^{1/2}\cos\theta_S+\epsilon_T^{1/2}\cos\theta_T}.$$

The longitudinal component of the electric field vector, parallel to $\mathbf{k}_T$, can be written in the form

$$E_{\|}^{T}\cos\beta=4\pi P_{\|}^{\mathrm{NLS}}\times\frac{\sin\alpha\sin^2\theta_S-\cos\alpha\cos(\theta_T-\theta_S)\sin(\theta_T+\theta_S)}{\epsilon_T\sin(\theta_T+\theta_S)}\times\exp\{i\omega c^{-1}z(\epsilon_S^{1/2}\cos\theta_S-\epsilon_T^{1/2}\cos\theta_T)\}. \quad (4.15)$$

Because of the presence of this longitudinal component, the energy flow in the transmitted ray will not be exactly in the direction of $\mathbf{k}_T$. In the limit of perfect phase matching, the longitudinal component is constant. From Eqs. (4.14) and (4.15), the electric field in the nonlinear medium is completely determined, both for perfect phase matching ($\theta_S=\theta_T$), and for phase mismatching. The solutions have, of course, assumed that the amplitudes of the incident waves remain unchanged by the nonlinearity. This is justified because the amplitude of the harmonic sum wave is relatively very small near the boundary. The solutions can be matched to the more general solutions for the infinite medium which allow for depletion of the power of the incident waves.

It is interesting to note that even in the case of purely longitudinal nonlinear polarization, $\alpha=0$, and perfect phase matching $\theta_S=\theta_T$, there is, nevertheless, a wave propagating into the medium with a transverse component. This wave does not increase with z; there is no amplification. It has its origin in the partial return at the boundary of the radiation from this longitudinal component which also gives rise to the reflected ray. One may also say that the nonlinear polarization induces a linear polarization, which is not purely longitudinal and may radiate. In the case of normal incidence ($\theta_T=\theta_S=0$), the radiation from the longitudinal component of the nonlinear polarization is completely absent.

C. Further Generalizations and an Example

The considerations of this section can, of course, be generalized immediately to higher harmonics. One simply determines P^{NLS} at the desired frequency of interest due to the presence of all waves incident on the linear medium. The equations of this section remain valid provided the angles θ_S, θ_T, and θ_R are properly determined in each situation with the method described in Sec. III.

The equations also remain valid for an absorbing medium. In this case, ϵ_T and ϵ_S are complex quantities, and the angles θ_T and θ_S are in general also complex. The angle of reflection given by Eq. (3.3) remains real. The fundamental and harmonic waves in the medium will decay with a characteristic length K_S^{-1} and K_T^{-1} given by

$$K_{S,T}=\mathrm{Im}[\omega c^{-1}(\epsilon_{S,T}'+i\epsilon_{S,T}'')^{1/2}].$$

The intensity of the reflected intensity will not change in order of magnitude if the absorption per wavelength in the nonlinear medium is small, $K\lambda\ll1$ or $\epsilon''\ll\epsilon'$. The general expressions Eqs. (4.5) and (4.13) can be decomposed in real and imaginary parts in a straightforward manner. There will be a phase shift, with respect to P^{NLS}, in the reflected harmonic amplitude from an absorbing medium. P^{NLS} itself is determined by light waves just inside the medium which are also phase shifted with respect to the incident wave. Only the expression for the reflected sum wave amplitude in the case of normal incidence will be written down explicitly as an example:

$$E^R(\theta_R=0)=-4\pi P^{\mathrm{NLS}}\{[\epsilon_T'(\omega_3)+i\epsilon_T''(\omega_3)]^{1/2}+[\epsilon_R(\omega_3)]^{1/2}\}^{-1}\{[\epsilon_T'(\omega_3)+i\epsilon_T''(\omega_3)]^{1/2}+(\omega_1/\omega_3)[\epsilon_T'(\omega_1)+i\epsilon_T''(\omega_1)]+(\omega_2/\omega_3)[\epsilon_T'(\omega_2)+i\epsilon_T''(\omega_2)]^{1/2}\}^{-1}. \quad (4.16)$$

The harmonic generation near the surface of a metal may be described by equations of this kind. The linear conductivity of the plasma can be formulated in terms of a complex dielectric constant and the nonlinear properties of the plasma are incorporated in P^{NLS}. It is given by Eq. (2.1) in terms of the light fields just inside the metal.

Another extension that can readily be made includes the case where there is also a wave at ω_3 incident on the nonlinear medium, besides the waves at ω_1 and ω_2.

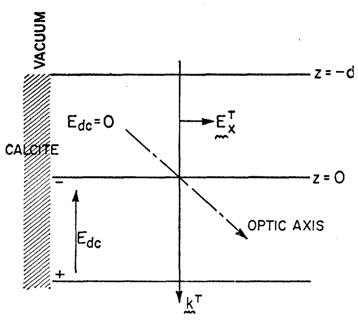

FIG. 6. Idealized geometry for the creation of second harmonics in a calcite crystal. In the absence of a dc electric field ($z<0$), the harmonic is generated by quadrupole matrix elements. In the presence of E_{dc} ($z>0$), dipole radiation is dominant. Interference effects occur at the boundary, $z=0$.

This situation is of importance if one desires to amplify further a signal at ω_3 rather than generate power in the absence of an incident signal.

There need not be a discontinuity in the linear dielectric constant at the boundary. The equations remain valid if $\epsilon_R=\epsilon_T$. A discontinuity in P^{NLS} alone occurs, for example, if the part of a crystal for $z>0$ is subjected to a strong dc electric field E_{dc}, while this field is absent for $z<0$. For simplicity, the light is assumed to enter normal to the boundary. This situation, shown in Fig. 6, represents an idealized geometry for a very interesting experiment on second harmonic generation in calcite recently reported by Terhune *et al.*[5]

The fundamental wave at ω_1, polarized in the x direction, creates a nonlinear polarization in the calcite crystal which has inversion symmetry at the second harmonic frequency by two terms

$$\mathbf{P}^{NLS}=\mathbf{Q}\vdots\mathbf{E}_1\nabla\mathbf{E}_1+\boldsymbol{\chi}\vdots\mathbf{E}_1\mathbf{E}_1\mathbf{E}_{dc}. \tag{4.17}$$

The nonvanishing components of the fourth-order tensors $\mathbf{Q}$ and $\boldsymbol{\chi}$ of interest in our geometry are the $x'x'x'x'$, $x'x'z'z'$, and $z'z'z'z'$ components. They will create a nonlinear polarization in the xz plane. The longitudinal component P_z^{NLS} is of little interest in the case of normal incidence, as shown by Eqs. (4.12), (4.14), and (4.15). The x component of the nonlinear polarization can be written as

$$P_x^{NLS}=iP_Q^{NLS} \quad \text{for} \quad z<0,$$
$$P_x^{NLS}=iP_Q^{NLS}+P^{NLS}(E_{dc}) \quad \text{for} \quad z>0.$$

The factor i takes account of the factor that the gradient operation produces a 90° phase shift. The polarization induced by the dc electric field is 90° out-of-phase with that produced by the quadrupole effect. This effect has already produced a second harmonic wave between $-d<z<0$, which is also incident on the boundary. If the condition of phase matching is approximately satisfied over the distance d, this incident amplitude is given by

$$E_x^i(2\omega)=-\frac{4\pi iP_Q^{NLS}}{2\epsilon(2\omega)^{1/2}[\epsilon^{1/2}(2\omega)+\epsilon^{1/2}(\omega)]}\times[1+ik_z(2\omega)d] \quad \text{for} \quad z<0. \tag{4.18}$$

It consists of the boundary wave created at $z=-d$ and the quadrupole amplified wave. The continuity conditions for E_x and H_y at $z=0$, where there is a discontinuity in P^{NLS},

$$\Delta P^{NLS}=P^{NLS}(z=+0)-P^{NLS}(z=-0)=P^{NLS}(E_{dc})$$

lead to a transmitted electric field,

$$E_x^T(z>0)=\frac{-4\pi iP_Q^{NLS}+[4\pi P_Q^{NLS}k_zd-4\pi P^{NLS}(E_{dc})]-4\pi(P^{NLS}(E_{dc})+iP_Q^{NLS})(ik_zz)}{2\epsilon^{1/2}(2\omega)[\epsilon^{1/2}(2\omega)+\epsilon^{1/2}(\omega)]}. \tag{4.19}$$

This expression shows how the boundary wave induced by the dc electric field may interfere with the wave which was amplified by the quadrupole effect in the region where the dc field is absent. This effect may explain why Terhune *et al.* observed a minimum in generated harmonic intensity[5] for a finite value of E_{dc}. It is not warranted to ascribe this minimum to the quadrupole effect and the balance to the E_{dc} effect. This would be correct only if E_{dc} could be applied uniformly in the whole calcite crystal. In that ideal geometry, the minimum in the generated harmonic intensity would be expected to occur indeed at $E_{dc}=0$. Our analysis applies only at the boundary with a discontinuity in E_{dc}, but similar interference effects can be expected in regions where a gradient of the dc electric field exists. A more detailed model consisting of a stack of plane-parallel slabs with different nonlinear (and linear) properties could be analyzed with the aid of the theory in Sec. VI.

V. TOTAL REFLECTION AND TRANSMISSION

Exponentially decaying or evanescent waves may occur even in nonabsorbing media. This phenomenon is known as total reflection in linear dielectrics.[8] It occurs when the law of refraction would yield a value of $\sin\theta_T>1$. There is a wider variety of circumstances in which one or more of the angles occurring in the nonlinear case, θ^R, θ^S, and θ^T, may assume a complex value, even though the dielectric constants are real. The various possibilities will be enumerated in this section for waves at the sum frequency $\omega_3=\omega_1+\omega_2$, and the difference frequency $\omega_{-3}=\omega_1-\omega_2$.

Case A: θ_1^T and θ_2^T are real. The incident waves are both transmitted into the nonlinear medium. The nonlinear polarization in the medium will be generated in the usual manner. The inhomogeneous wave has a real propagation vector, $\sin\theta_S<1$. Inspection of Eq. (3.3) shows that in the case of normal dispersion,

$\epsilon_3^R > \epsilon_1^R$ and ϵ_2^R, and $\epsilon_3^T > \epsilon_1^T$ and ϵ_2^T, the angles θ_3^R and θ_3^T will always be real. The situation is quite different for the difference frequency. The general expressions for the angles are

$$\begin{aligned}\omega_{-3}^2\epsilon_{-3}^R \sin^2\theta_{-3}^R &= \omega_{-3}^2\epsilon_{-3}^T \sin^2\theta_{-3}^T \\ &= \omega_1^2\epsilon_1^R \sin^2\theta_1^i + \omega_2^2\epsilon_2^R \sin^2\theta_2^i \\ &\quad - 2\omega_1\omega_2(\epsilon_1^R)^{1/2}(\epsilon_2^R)^{1/2} \sin\theta_1^i \sin\theta_2^i \cos\phi. \qquad (5.1)\end{aligned}$$

The smaller the difference frequency ω_{-3}, the larger the probability that the waves at this frequency cannot be radiated. This probability is especially large, if $\cos\phi < 0$, i.e., if the two incident rays approach the boundary from opposite sides of the normal, and if the angles of incidence are close to 90°.

Whenever $\sin\theta_R$ or $\sin\theta_T$, as determined from Eq. (5.1), is larger than unity, the wave will exhibit an exponentially decaying characteristic in the linear or nonlinear medium, respectively. The evanescent reflected or transmitted wave at ω_{-3} will have the following spatial dependence

$$\exp[i(k_{1x}^i - k_{2x}^i)x + i(k_{1y}^i - k_{2y}^i)y] \times \exp[-(\sin^2\theta_{-3}^{R,T} - 1)^{1/2}\omega_{-3}c(\epsilon_{-3}^{R,T})^{1/2}z].$$

The x and y dependence has still the same oscillatory character, but the waves evanesce in the z direction and are essentially confined to a region of a few wavelengths near the boundary. Four subcases may be distinguished.

*A*1. $\sin\theta_S < 1$, $\sin\theta_T < 1$, $\sin\theta_R < 1$. This is the normal situation, which was discussed extensively in the preceding sections. All waves propagate.

*A*2. $\sin\theta_S < 1$, $\sin\theta_T < 1$, but $\sin\theta_R > 1$. This case can occur for the difference frequency ω_{-3}, if $\epsilon_{-3}^R < \epsilon_{-3}^T$. There is no reflected wave at ω_{-3}. The difference frequency is totally transmitted. The amplitude of the transmitted wave is still given by Eqs. (4.8), (4.14), and (4.15). Since $\sin^2\theta_R > 1$, $\cos\theta_R = i(\sin^2\theta_R - 1)$ is pure imaginary. Equation (4.5) may be rewritten as

$$E_\perp^R = \frac{-4\pi P_\perp^{\mathrm{NLS}} \sin^2\theta_T \sin\theta_S}{\sin(\theta_S+\theta_T)\sin\theta_R[\sin\theta_R\cos\theta_T + i(\sin^2\theta_R - 1)^{1/2}\sin\theta_T]}. \qquad (5.2)$$

There is no particular interest in the reflected amplitude as such because it decays rapidly away from the boundary. If Eq. (5.2) is combined with Eq. (4.8), it is evident that the transmitted wave has a phase shift with respect to the nonlinear polarization. The amplified part of the transmitted wave is not affected by the frustrated reflection.

Similar conclusions may be drawn for the transmitted wave polarized in the plane of transmission. The amplitudes are still given by Eqs. (4.14) and (4.15). A substitution in the denominator of the first term on the right-hand side of Eq. (4.14),

$$\sin(\theta_T+\theta_R)\cos(\theta_T-\theta_R) = \sin\theta_T\cos\theta_T + i\sin\theta_R(\sin^2\theta_R - 1)^{1/2} \qquad (5.3)$$

shows the phase shift of the transmitted amplitude with respect to $P_\parallel^{\mathrm{NLS}}$. The amplified part and the longitudinal component [Eq. (4.15)] are not affected by the frustrated reflection.

*A*3. $\sin\theta_S < 1$, $\sin\theta_R < 1$, $\sin\theta_T > 1$. This situation can occur for the difference frequency, if $\epsilon_{-3}^R > \epsilon_{-3}^T$. In this case $\cos\theta_{-3}^T = i(\sin^2\theta_{-3}^T - 1)^{1/2}$ is pure imaginary. The reflected amplitude for perpendicular polarization is still given by Eqs. (4.5) and (4.13). These expressions can readily be decomposed in their real and imaginary parts, but the algebraic results will not be reproduced here. There will be a phase shift, because the reflected amplitude is now complex. Its order of magnitude is not changed by the fact that the homogeneous wave is not transmitted.

There will still be a transmitted intensity because the inhomogeneous wave propagates. At a distance more than a few wavelengths from the boundary the transmitted wave will be given by

$$E_\perp^T = [4\pi P_\perp^{\mathrm{NLS}}/(\epsilon_S - \epsilon_T)] \exp i(\mathbf{k}_S \cdot \mathbf{r} - \omega_{-3}t). \qquad (5.4)$$

A similar expression exists for the parallel polarization. Matching of the phase velocities does not exist, since one must have $\epsilon_S - \epsilon_T > 0$, if $\sin\theta_S < 1$, and $\sin\theta_T > 1$.

There is no particular advantage to try and make $\epsilon_S \to \epsilon_T$, since for that limit one must restore to Eq. (5.4) the inhomogeneous, evanescent solution that decays slower and slower as $\epsilon_S \to \epsilon_T$ for $\sin\theta_S < 1$.

*A*4. $\sin\theta_S < 1$, $\sin\theta_R > 1$, and $\sin\theta_T > 1$. Only the inhomogeneous transmitted wave is not evanescent in this case. The amplitude of the transmitted wave away from the boundary is again given by Eq. (5.4).

Case *B*. Both incident waves are totally reflected, $\sin\theta_1^T > 1$ and $\sin\theta_2^T > 1$. In this case, which can occur if the linear medium is optically more dense than the nonlinear medium, the inhomogeneous wave is always evanescent, $\sin\theta_S > 1$. The nonlinear polarization decreases exponentially away from the boundary, but the polarization at the sum or difference frequency, restricted to a surface layer of about one wavelength thick, may produce traveling waves both in reflection and transmission. The following situations should be distinguished.

*B*1. $\sin\theta_S > 1$, $\sin\theta_T > 1$, $\sin\theta_R < 1$. In this case the waves at sum and difference frequencies are also totally reflected. It will usually occur when a single fundamental wave is incident and totally reflected. The second harmonic will, e.g., have an angle θ_T with $\sin\theta_T(2\omega) = [\epsilon_T^{1/2}(\omega)/\epsilon_T^{1/2}(2\omega)] \sin\theta_S$ larger than unity, unless an unusual dispersion is present. The intensity of reflected harmonic is again given by Eq. (4.5) or

Eq. (4.13), where now both $\cos\theta_S$ and $\cos\theta_T$ are purely imaginary. There will be phase shifts with respect to P^{NLS}, but the important point is that the intensity of the reflected harmonic has the same order of magnitude, if the incident wave is totally reflected or transmitted. It may be possible to generate second and higher harmonics by repeated total reflection from nonlinear dielectric surfaces.

*B*2. $\sin\theta_S > 1$, but $\sin\theta_T < 1$ and $\sin\theta_R < 1$. This case could occur, for example, if the sum wave frequency is created by two totally reflected incident waves, hitting the boundary from opposite sides. Since the inhomogeneous wave dies out rapidly, the reflected and transmitted field amplitudes are given by Eqs. (4.5) and (4.2), respectively, with $\cos\theta_S$ pure imaginary. The waves polarized in the plane of reflection can be treated in a similar manner.

*B*3. $\sin\theta_S > 1$, $\sin\theta_T < 1$, $\sin\theta_R > 1$. Since the first condition requires $\epsilon_R(\omega_1 \text{ and } \omega_2) > \epsilon_T(\omega_1 \text{ and } \omega_2)$, and the last two $\epsilon_R(\omega_3) < \epsilon_T(\omega_3)$, this situation would be extremely rare in an isotropic medium. It could occur by special choice of ordinary and extraordinary rays in an anisotropic medium.

*B*4. $\sin\theta_S > 1$, $\sin\theta_T > 1$, $\sin\theta_R > 1$. This case is not of much experimental interest since all harmonic waves are evanescent.

Case *C*. $\sin\theta_S$ complex. Finally, the situations should be considered in which one of the incident waves (at ω_1) is transmitted, but the wave at ω_2 is totally reflected. The nonlinear polarization created at the sum or difference frequency will again drop exponentially away from the boundary. The spatial dependence of $P^{\mathrm{NLS}}(\omega_3)$ is, e.g., given by

$$\exp[i(k_{1x}{}^i + k_{2x}{}^i)x + i(k_{1y}{}^i + k_{2y}{}^i)y] \times \exp[i\omega c^{-1}(\epsilon_1{}^T)^{1/2}(\cos\theta_1{}^T)z] \times \exp[-\omega c^{-1}(\epsilon_2{}^T)^{1/2}(\sin^2\theta_2{}^T - 1)^{1/2}z].$$

A complex factor now multiplies z in the exponential function. Again four subcases should be distinguished:

*C*1. $\sin\theta_S$ complex, $\sin\theta_T > 1$, $\sin\theta_R < 1$,

*C*2. $\sin\theta_S$ complex, $\sin\theta_T < 1$, $\sin\theta_R < 1$,

*C*3. $\sin\theta_S$ complex, $\sin\theta_T < 1$, $\sin\theta_R > 1$,

*C*4. $\sin\theta_S$ complex, $\sin\theta_T > 1$, $\sin\theta_R > 1$.

The discussion of the intensity of the reflected and transmitted is quite analogous to the corresponding cases *B*. The transmitted intensity is again determined by the homogeneous wave, since the inhomogeneous intensity drops exponentially. The generalized Fresnel equations for E^R and $\mathcal{E}^T$ can again be used, in which $\sin\theta_S$ and $\cos\theta_S$ are now complex quantities.

$$\cos\theta_S = i\omega c^{-1}\epsilon_2{}^{1/2}(\sin^2\theta_2{}^T - 1)^{1/2} + \omega c^{-1}\epsilon_1{}^{1/2}\cos\theta_1{}^T.$$

No further computational details need to be supplied.

VI. THE NONLINEAR PLANE-PARALLEL PLATE

Consider an infinite slab M of a nonlinear dielectric medium with boundaries at $z=0$ and $z=d$, embedded between two linear dielectrics R and T. Two linear waves at ω_1 and ω_2 are incident from the medium R for $z<0$, as schematically shown in Fig. 7. They will create forward moving waves $E_{1,M}$ and $E_{2,M}$ and backward moving waves $E_{1,M}{}'$ and $E_{2,M}{}'$ in the nonlinear medium. These waves can be calculated according to the usual linear theory. They will produce a nonlinear polarization at the sum frequency ω_3.

In general, four inhomogeneous waves will be associated with this nonlinear polarization.

$$\begin{aligned}\mathbf{P}^{\mathrm{NLS}}(\omega_3) = \chi \exp[i(k_{1x}+k_{2x})x + i(k_{1y}+k_{2y})y] \\ \times\{\mathbf{E}_{1,M}\mathbf{E}_{2,M}\exp[i(k_{1,z}{}^M + k_{2,z}{}^M)z] \\ + \mathbf{E}_{1,M}\mathbf{E}_{2,M}{}'\exp[i(k_{1,z}{}^M - k_{2,z}{}^M)z] \\ + \mathbf{E}_{1,M}{}'\mathbf{E}_{2,M}\exp[i(-k_{1,z}{}^M + k_{2,z}{}^M)z] \\ + \mathbf{E}_{1,M}{}'\mathbf{E}_{2,M}{}'\exp[-i(k_{1,z}{}^M + k_{2,z}{}^M)z]\}. \quad (6.1)\end{aligned}$$

Note that these inhomogeneous waves all have the same x and y dependence. The boundary conditions at $z=0$ and $z=d$ can be met if one adds four waves which satisfy the homogeneous wave equation at the frequency ω_3 with the same x and y dependence. These waves which all lie in the same plane with the normal of the slab are also shown in Fig. 7. It is again possible to treat separately the case in which the $\mathbf{E}(\omega_3)$ and the nonlinear polarization are perpendicular to this plane, and the case in which they are parallel to this plane.

It should be noted that the symmetry which exists in the linear case between waves going from medium A to B or from B to A is lost in the nonlinear case. If the light approaches the boundary from inside the nonlinear medium, one always must have both a homogeneous and an inhomogeneous wave incident, whereas in the linear medium there is only the homogeneous wave. The problem of the nonlinear slab clearly presents itself in many experimental situations. Harmonic generation is usually accomplished in a slab of nonlinear material. The creation of harmonic waves inside a laser crystal or Fabry-Pérot interferometer involves the same situation. Although only the waves at the sum frequency will be considered explicitly, the method is equally

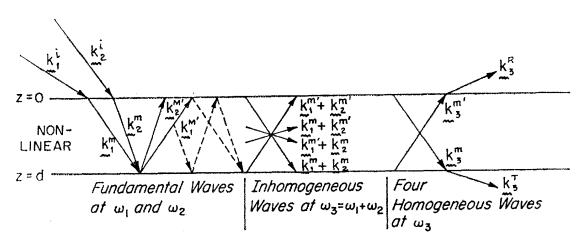

FIG. 7. Waves in the nonlinear plane parallel slab. Fundamental waves $E_1{}^M$ and $E_1{}^{M'}$ at ω_1 and $E_2{}^M$ and $E_2{}^{M'}$ at ω_2 give rise to inhomogeneous waves at $\omega_3=\omega_1+\omega_2$. The four homogeneous waves at ω_3 include a reflected ray E^R and transmitted ray E^T from the slab at the sum frequency ω_3.

applicable to higher harmonics, the difference frequency, etc. One only has to focus attention on the components of the nonlinear polarization [Eq. (6.1)] at the corresponding frequencies. The method presented here is, however, restricted to "weak harmonic generation." The incident fields at ω_1 and ω_2 in the slab are considered to be given as fixed parameters by the linear theory. They are not appreciably attenuated by the nonlinear processes. The interest will, of course, center on the waves $E_3{}^R$ and $E_3{}^T$ that emerge on either side of the slab. In order to avoid nonessential algebraic effort, only one inhomogeneous wave will be retained, the first term on the right-hand side of Eq. (6.1). For small linear reflectance of the dielectric, $E_{1,M}'<E_{1,M}$ and $E_{2,M}'<E_{2,M}$, this will approximate the correct result closely. For high reflectance the equations can be generalized without difficulty. The case where there is an incident wave at ω_3 in the medium R as well, could also be included in a straightforward manner. The propagation constant for the inhomogeneous wave is again written as $\omega_3 c^{-1}\epsilon_S{}^{1/2}$. The subscript 3 will henceforth be dropped, since all quantities will refer to the sum frequency.

With these assumptions the boundary conditions in the case of perpendicular polarization can be written as

$$E_y(z=0)=E_R=E_M+E_M'+4\pi P^{\mathrm{NLS}}(\epsilon_S-\epsilon_M)^{-1}, \quad (6.2)$$

$$E_y(z=d)=E_T=E_M\exp(i\phi_M)+E_M'\exp(-i\phi_M) +4\pi P^{\mathrm{NLS}}(\epsilon_S-\epsilon_M)^{-1}\exp(i\phi_S), \quad (6.3)$$

$$H_x(z=0)=-\epsilon_R{}^{1/2}\cos\theta_R E_R=\epsilon_M{}^{1/2}\cos\theta_M(E_M-E_M') +4\pi\epsilon_S{}^{1/2}\cos\theta_S P^{\mathrm{NLS}}(\epsilon_S-\epsilon_M)^{-1}, \quad (6.4)$$

$$H_x(z=d)=\epsilon_T{}^{1/2}\cos\theta_T E_T=\epsilon_M{}^{1/2}\cos\theta_M[E_M\exp(i\phi_M) -E_M'\exp(-i\phi_M)]+4\pi\epsilon_S{}^{1/2}\cos\theta_S \times P^{\mathrm{NLS}}(\epsilon_S-\epsilon_M)^{-1}\exp(i\phi_S), \quad (6.5)$$

where ϕ_S and ϕ_M are the phase shifts of the inhomogeneous and homogeneous waves, respectively,

$$\phi_S=\epsilon_S{}^{1/2}\omega c^{-1}d\cos\theta_S,\quad \phi_M=\epsilon_M{}^{1/2}\omega c^{-1}d\cos\theta_M. \quad (6.6)$$

This is a set of four simultaneous linear equations that can be solved for the four homogeneous wave amplitudes and phases.

The reflected and transmitted harmonic waves have the following complex amplitudes,

$$E_\perp{}^R=4\pi P^{\mathrm{NLS}}D^{-1}[(\epsilon_S{}^{1/2}\cos\theta_S-\epsilon_T{}^{1/2}\cos\theta_T)(\cos\phi_M-\cos\phi_S)(\epsilon_M-\epsilon_S)^{-1} +i\epsilon_T{}^{1/2}\cos\theta_T(\epsilon_M{}^{1/2}\cos\theta_M)^{-1}(\epsilon_M{}^{1/2}\cos\theta_M\sin\phi_S-\epsilon_S{}^{1/2}\cos\theta_S\sin\phi_M)(\epsilon_M-\epsilon_S)^{-1} +i(\epsilon_M{}^{1/2}\cos\theta_M\sin\phi_M-\epsilon_S{}^{1/2}\cos\theta_S\sin\phi_S)(\epsilon_M-\epsilon_S)^{-1}], \quad (6.7)$$

$$E_\perp{}^T=4\pi P^{\mathrm{NLS}}D^{-1}[-(\epsilon_R{}^{1/2}\cos\theta_R+\epsilon_S{}^{1/2}\cos\theta_S)(\cos\phi_M-\cos\phi_S)(\epsilon_M-\epsilon_S)^{-1} -i\epsilon_R{}^{1/2}\cos\theta_R(\epsilon_M{}^{1/2}\cos\theta_M)^{-1}(\epsilon_M{}^{1/2}\cos\theta_M\sin\phi_S-\epsilon_S{}^{1/2}\cos\theta_S\sin\phi_M)(\epsilon_M-\epsilon_S)^{-1} +i(\epsilon_M{}^{1/2}\cos\theta_M\sin\phi_M-\epsilon_S{}^{1/2}\cos\theta_S\sin\phi_S)(\epsilon_M-\epsilon_S)^{-1}], \quad (6.8)$$

where

$$D=\cos\phi_M(\epsilon_T{}^{1/2}\cos\theta_T+\epsilon_R{}^{1/2}\cos\theta_R)-i\sin\phi_M[\epsilon_R{}^{1/2}\epsilon_T{}^{1/2}\cos\theta_R\cos\theta_T(\epsilon_M{}^{1/2}\cos\theta_M)^{-1}+\epsilon_M{}^{1/2}\cos\theta_M]. \quad (6.9)$$

The terms in the numerator of Eqs. (6.7) and (6.8) are grouped so that each has a finite limit as ϵ_M approaches ϵ_S. For the limiting case of perfect matching

$$E_\perp{}^R(\epsilon_M=\epsilon_S)=i2\pi P^{\mathrm{NLS}}D^{-1}\{\omega dc^{-1}[1-\epsilon_T{}^{1/2}\cos\theta_T(\epsilon_M{}^{1/2}\cos\theta_M)^{-1}]\exp(i\phi_M) +\sin\phi_M(\epsilon_T{}^{1/2}\cos\theta_T+\epsilon_M{}^{1/2}\cos\theta_M)(\epsilon_M{}^{1/2}\cos\theta_M)^{-2}\}, \quad (6.10)$$

$$E_\perp{}^T(\epsilon_M=\epsilon_S)=i2\pi P^{\mathrm{NLS}}D^{-1}\exp(-i\phi_M)\{\sin\phi_M(\epsilon_M{}^{1/2}\cos\theta_M)^{-1}[1-\epsilon_R{}^{1/2}\cos\theta_R(\epsilon_M{}^{1/2}\cos\theta_M)^{-1}]\exp(i\phi_M) +\omega dc^{-1}[1+\epsilon_R{}^{1/2}\cos\theta_R(\epsilon_M{}^{1/2}\cos\theta_M)^{-1}]\}. \quad (6.11)$$

Both the transmitted and reflected waves contain terms proportional to the thickness of the nonlinear dielectric. For the reflected wave this arises from the forward amplified wave reflected from the discontinuity at the second surface. When $\epsilon_T=\epsilon_M$ there is no discontinuity and this term vanishes. In this case the amplitude of the reflected wave depends on the thickness of the slab as $\sin\phi_M$ and the phase is determined through the denominator, D, given by Eq. (6.9). The reflected wave varies between zero and twice the value given by Eq. (4.5) for reflection from a semi-infinite medium. This is reasonable since additional layers of dipoles interfere either constructively or destructively as the thickness of the slab increases. The average amplitude for infinite thickness is just one-half the amplitude for optimum thickness.

The transmitted wave has the expected term proportional to thickness, and in addition, there is the boundary wave from the first surface. If $\epsilon_R=\epsilon_M$, this wave, of course, vanishes.

In the limit that the layer is thin compared to a wavelength, the general expressions [Eqs. (6.7) and (6.8)] simplify to

$$E_\perp{}^T\approx E_\perp{}^R\approx i4\pi P^{\mathrm{NLS}}(\omega dc^{-1}) \times(\epsilon_T{}^{1/2}\cos\theta_T+\epsilon_R{}^{1/2}\cos\theta_R)^{-1}. \quad (6.12)$$

The amplitudes of the waves radiated in the forward (transmitted) and the backward (reflected) directions are equal for a thin layer. The intensities of the two waves are proportional to the square of the thickness, since all the atoms radiate coherently. One may also say that the harmonic waves generated at the front and back surfaces due to the discontinuity in the nonlinear part of the dielectric constant $\chi(\omega_3=\omega_1+\omega_2)$ interfere destructively. This is similar to the interference in very thin linear film when the discontinuity is in $\boldsymbol{\varepsilon}$.

If the reflection coefficient for the fundamental waves is large, as in a Fabry-Perot interferometer, one has to take the other inhomogeneous solution of Eq. (6.1) into account. Algebraically, this amounts to a summation over the index S in Eqs. (6.7) and (6.8) and their limiting cases.

The case of parallel polarization can be treated in the same manner. The boundary conditions are:

$$E_x(z=0)=-E_R\cos\theta_R=(E_M-E_M')\cos\theta_M-4\pi P^{\mathrm{NLS}}\sin\alpha\cos\theta_S(\epsilon_M-\epsilon_S)^{-1}-4\pi P^{\mathrm{NLS}}\cos\alpha\sin\theta_S\epsilon_M^{-1}, \tag{6.13}$$

$$E_z(z=d)=E_T\cos\theta_T=[E_M\exp(i\phi_M)-E_M'\exp(-i\phi_M)]\cos\theta_M$$
$$-4\pi P^{\mathrm{NLS}}\sin\alpha\cos\theta_S(\epsilon_M-\epsilon_S)^{-1}\exp(i\phi_S)-4\pi P^{\mathrm{NLS}}\cos\alpha\sin\theta_S\epsilon_M^{-1}\exp(i\phi_S), \tag{6.14}$$

$$H_y(z=0)=\epsilon_R^{1/2}E_R=\epsilon_M^{1/2}(E_M+E_M')-4\pi P^{\mathrm{NLS}}\sin\alpha\epsilon_S^{1/2}(\epsilon_M-\epsilon_S)^{-1}, \tag{6.15}$$

$$H_y(z=d)=\epsilon_T^{1/2}E_T=\epsilon_M^{1/2}[E_M\exp(i\phi_M)-E_M'\exp(-i\phi_M)]-4\pi P^{\mathrm{NLS}}\sin\alpha\epsilon_S^{1/2}(\epsilon_M-\epsilon_S)^{-1}\exp(i\phi_S). \tag{6.16}$$

The solutions for the amplitudes of the reflected and transmitted waves are

$$\begin{aligned}E_{\parallel}^R=4\pi P^{\mathrm{NLS}}\sin\alpha D^{-1}[&(\epsilon_T^{1/2}\cos\theta_S-\epsilon_S^{1/2}\cos\theta_T)(\cos\phi_M-\cos\phi_S)(\epsilon_M-\epsilon_S)^{-1}\\&+i(\epsilon_T/\epsilon_M)^{1/2}(\epsilon_S^{1/2}\sin\phi_M\cos\theta_M-\epsilon_M^{1/2}\cos\theta_S\sin\phi_S)(\epsilon_M-\epsilon_S)^{-1}\\&+i(\cos\theta_T/\cos\theta_M)(\epsilon_S^{1/2}\sin\phi_S\cos\theta_M-\epsilon_M^{1/2}\cos\theta_S\sin\phi_M)(\epsilon_M-\epsilon_S)^{-1}]\\&+4\pi P^{\mathrm{NLS}}\cos\alpha\epsilon_M^{-1}D^{-1}[\epsilon_T^{1/2}\sin\theta_S(\cos\phi_M-\cos\phi_S)\\&\qquad-i(\sin\theta_S/\cos\theta_M)(\epsilon_T^{1/2}\sin\phi_S\cos\theta_M+\epsilon_M^{1/2}\sin\phi_M\cos\theta_T)],\end{aligned} \tag{6.17}$$

$$\begin{aligned}E_{\parallel}^T=4\pi P^{\mathrm{NLS}}\sin\alpha D^{-1}\exp(i\phi_S)[&-(\epsilon_R^{1/2}\cos\theta_S+\epsilon_S^{1/2}\cos\theta_R)(\cos\phi_M-\cos\phi_S)(\epsilon_M-\epsilon_S)^{-1}\\&+i(\epsilon_R/\epsilon_M)^{1/2}(\epsilon_S^{1/2}\sin\phi_M\cos\theta_M-\epsilon_M^{1/2}\cos\theta_S\sin\phi_S)(\epsilon_M-\epsilon_S)^{-1}\\&-i(\cos\theta_R/\cos\theta_M)(\epsilon_S^{1/2}\sin\phi_S\cos\theta_M-\epsilon_M^{1/2}\cos\theta_S\sin\phi_M)(\epsilon_M-\epsilon_S)^{-1}]\\&+4\pi P^{\mathrm{NLS}}\cos\alpha\epsilon_M^{-1}D^{-1}\exp(i\phi_S)[-\epsilon_R^{1/2}\sin\theta_S(\cos\phi_M-\cos\phi_S)\\&\qquad-i(\sin\theta_S/\cos\theta_M)(\epsilon_R^{1/2}\sin\phi_S\cos\theta_M-\epsilon_M^{1/2}\sin\phi_M\cos\theta_R)],\end{aligned} \tag{6.18}$$

where

$$D=\cos\phi_M(\epsilon_R^{1/2}\cos\theta_T+\epsilon_T^{1/2}\cos\theta_R)-i\sin\phi_M(\epsilon_M^{1/2}\cos\theta_M)^{-1}(\epsilon_M\cos\theta_R\cos\theta_T+(\epsilon_R\epsilon_T)^{1/2}\cos^2\theta_M). \tag{6.19}$$

The numerators in Eqs. (6.17) and (6.18) are again grouped in terms that have finite limits as ϵ_M approaches ϵ_S. For the limiting case of perfect matching

$$\begin{aligned}E_{\parallel}^R(\epsilon_S=\epsilon_M)=i2\pi P^{\mathrm{NLS}}D^{-1}\{&\omega dc^{-1}\sin\alpha[(\epsilon_T/\epsilon_M)^{1/2}-(\cos\theta_T/\cos\theta_M)]\exp(i\phi_M)\\&-\sin\phi_M(\epsilon_M^{1/2}\cos\theta_M)^{-1}[(\epsilon_T/\epsilon_M)^{1/2}+(\cos\theta_T/\cos\theta_M)]\sin(2\theta_M+\alpha)\},\end{aligned} \tag{6.20}$$

$$\begin{aligned}E_{\parallel}^T(\epsilon_S=\epsilon_M)=i2\pi P^{\mathrm{NLS}}D^{-1}\{&\omega dc^{-1}\sin\alpha[(\epsilon_R/\epsilon_M)^{1/2}+(\cos\theta_R/\cos\theta_M)]\\&-\sin\phi_M(\epsilon_M^{1/2}\cos\theta_M)^{-1}[(\epsilon_R/\epsilon_M)^{1/2}-(\cos\theta_R/\cos\theta_M)]\sin(2\theta_M+\alpha)\exp(i\phi_M)\}.\end{aligned} \tag{6.21}$$

In the limit of thicknesses small compared to a wavelength, Eqs. (6.17) and (6.18) become

$$E_{\parallel}^R=-i4\pi P^{\mathrm{NLS}}\omega dc^{-1}[(\epsilon_T/\epsilon_M)^{1/2}\sin\theta_M\cos(\theta_S+\alpha)+\cos\theta_T\sin(\theta_S+\alpha)](\epsilon_T^{1/2}\cos\theta_R+\epsilon_R^{1/2}\cos\theta_T)^{-1}, \tag{6.22}$$

$$E_{\parallel}^T=-i4\pi P^{\mathrm{NLS}}\omega dc^{-1}[(\epsilon_R/\epsilon_M)^{1/2}\sin\theta_M\cos(\theta_S+\alpha)-\cos\theta_R\sin(\theta_S+\alpha)](\epsilon_R^{1/2}\cos\theta_T+\epsilon_T^{1/2}\cos\theta_R)^{-1}. \tag{6.23}$$

The discussion for the perpendicular polarization, following Eqs. (6.10), (6.11), and (6.12) can be carried over to the parallel case. The symmetry between the forward and backward radiated fields is spoiled in the case of parallel polarization.

Note also the occurrence of a Brewster angle in the case of perfect matching ($\epsilon_S=\epsilon_M$). If $2\theta_M+\alpha=\pi$, there is no backward wave generated in the medium. If, in addition, the reflection of the forward wave at the second boundary is suppressed by taking $\epsilon_T=\epsilon_M$, the reflected intensity is zero. For a linear plane parallel slab, complete transmission will occur simultaneously at both the front and the back surface, if Brewster's condition is satisfied. This symmetry does not exist in the nonlinear slab.

The same physical explanation for Brewster's angle may be given as in the case of the semi-infinite medium. If the total polarization (linear+nonlinear) of the medium is parallel to the direction of reflected ray, it must have vanishing intensity. This will be illustrated for the case of a very thin film in vacuum. If the reflected wave is required to vanish, the continuity conditions on D and E determine the total polarization $(\mathbf{D}-\mathbf{E})/4\pi$ inside the medium. The components of this total polarization can be expressed in terms of P^{NLS} as follows:

$$P_{x,y}=P_{x,y}{}^{\mathrm{NLS}}, \quad P_z=P_z{}^{\mathrm{NLS}}/\epsilon_M. \tag{6.24}$$

Since P^{NLS} makes an angle $\theta_S+\alpha$ with the boundary normal from R into the nonlinear medium M, the total polarization makes an angle ζ with the normal whose tangent is a factor ϵ_M larger. Brewster's condition is $\zeta+\theta_R=\pi$ or

$$\tan\theta_R=-\tan\zeta=-\epsilon_M{}^{-1}\tan(\theta_S+\alpha). \tag{6.25}$$

For $\epsilon_T=\epsilon_R=1$, one has $(\epsilon_T/\epsilon_M)^{1/2}\sin\theta_M=\epsilon_M{}^{-1}\sin\theta_T$. Equation (6.25) is therefore equivalent to the condition that the expression [Eq. (6.22)] vanishes.

VII. INTEGRAL EQUATION METHOD FOR WAVE PROPAGATION IN A NONLINEAR MEDIUM

From a microscopic physical point of view there exists only the incident radiation field in vacuum and the dipolar microscopic radiation fields in vacuum emanating from each atomic dipole. Ewald and Oseen have shown for the linear dielectric that the properly retarded atomic dipole fields lead, on integration, to exactly the same results as the combination of Maxwell's equations coupled with the Lorentz treatment of quasi-static local fields. In a similar manner the treatment of ABDP, which extended the Maxwell-Lorentz method to nonlinear dielectrics, can be justified by an extension of the Ewald-Oseen integral equation method. The account and notation employed by Born and Wolf in the linear case will be followed closely.[9] As in the linear case, the reflected and refracted waves at the boundary of a nonlinear medium also follow correctly from the integral equation method.

A semi-infinite dielectric $z\leq 0$, in contact with vacuum $z>0$, has a polarization density $\mathbf{P}(r,t)$ consisting of a linear and nonlinear contribution. The nonlinear polarization results from the nonlinear polarizability of a unit cell as discussed by ABDP. The nonlinear polarization of the ith cell is $\mathcal{P}^{\mathrm{NL}}(t,r_i)$. If there are N cells per unit volume, the nonlinear polarization density is $P^{\mathrm{NL}}(r,t)=N\mathcal{P}^{\mathrm{NL}}(t,r)$. In the most general case of an incident field $E^i(r,t)$ the total electric field at any point r on the medium can be written as

$$\mathbf{E}'(r,t)=\mathbf{E}^{(i)}+\int_\sigma^\Sigma \nabla\times\nabla\times[\mathbf{P}(r',t-R/c)/R]dV', \tag{7.1}$$

where σ is a small surface surrounding the point r and Σ is the outer surface of the dielectric. Consider the component of Eq. (7.1) at some frequency ω for which $P^{\mathrm{NL}}\neq 0$. Take as a trial solution

$$\begin{aligned}\mathbf{E}'(r,\omega)&=\mathbf{Q}^a(r)+\mathbf{Q}^b(r),\\ \mathbf{E}^i(r,\omega)&=\mathbf{Q}^i(r),\\ \mathbf{P}^{\mathrm{NL}}(r,\omega)&=\mathbf{F}(r)\end{aligned} \tag{7.2}$$

where the fields on the right-hand side satisfy the equations

$$\begin{aligned}\nabla^2\mathbf{Q}^a+\epsilon_S(\omega/c)^2\mathbf{Q}^a&=0,\\ \nabla^2\mathbf{Q}^b+\epsilon(\omega/c)^2\mathbf{Q}^b&=0,\\ \nabla^2\mathbf{Q}^i+(\omega/c)^2\mathbf{Q}^i&=0,\\ \nabla^2\mathbf{F}+\epsilon_S(\omega/c)^2\mathbf{F}&=0.\end{aligned} \tag{7.3}$$

The velocity of the source wave in the medium, which defines ϵ_S, can be determined from the solution of the linear problem for the waves at incident frequencies, different from ω. The linear dielectric constant at ω is given by ϵ. The amplitude of the total polarization per unit volume appearing in the integral of Eq. (7.1) is

$$\mathbf{P}(r',\omega)=N\alpha[\mathbf{Q}^a+\mathbf{Q}^b]+\mathbf{F}, \tag{7.4}$$

where α is the polarizability of a unit cell at frequency ω and N is the number of unit cells per cm³.

Substitution of Eqs. (7.2) and (7.4) into Eq. (7.1) leads, with the procedure of Born and Wolf, to

$$\begin{aligned}\mathbf{Q}^a(r)+\mathbf{Q}^b(r)&=\mathbf{Q}^i(r)+\tfrac{4}{3}\pi N\alpha(\epsilon+2)/(\epsilon-1)\mathbf{Q}^b(r)\\ &+\frac{4}{3}\pi\frac{\epsilon_S+2}{\epsilon_S-1}[N\alpha\mathbf{Q}^a(r)+\mathbf{F}(r)]\\ &+\frac{4\pi}{\epsilon_S-1}\left(\frac{c}{\omega}\right)^2\nabla[\nabla\cdot(\mathbf{F}(r)+N\alpha\mathbf{Q}^a(r))]\\ &+\left(\frac{c}{\omega}\right)^2\nabla\times\nabla\times\int_\Sigma d\mathbf{S}'\cdot\left\{[\nabla G(R)]\left[\frac{N\alpha}{\epsilon-1}\mathbf{Q}^b(r')\right.\right.\\ &\left.+\frac{N\alpha\mathbf{Q}^a(r')+\mathbf{F}(r')}{\epsilon_S-1}\right]-G(R)\nabla\left[\frac{N\alpha}{\epsilon-1}\mathbf{Q}^b(r')\right.\\ &\left.\left.+\frac{N\alpha\mathbf{Q}^a(r')+\mathbf{F}(r')}{\epsilon_S-1}\right]\right\},\end{aligned} \tag{7.5}$$

where $G(R)=(1/R)\exp[i(\omega/c)R]$. The third term on the right of the equal sign is necessary since, in general, $\nabla\cdot\mathbf{F}$ and $\nabla\cdot\mathbf{Q}^a$ are not zero.

Equation (7.5) has terms propagating with speeds c, $c(\epsilon)^{-1/2}$, and $c(\epsilon_S)^{-1/2}$. If the identity is to hold for all points in the medium, these three types of terms must vanish separately.

Terms propagating with speed c

$$0=\mathbf{Q}^i+\left(\frac{c}{\omega}\right)^2\nabla\times\nabla\times\int_\Sigma d\mathbf{S}'\cdot\{\quad\}; \tag{7.6a}$$

terms propagating with speed $c(\epsilon)^{-1/2}$

$$\mathbf{Q}^b=\frac{4\pi}{3}N\alpha\frac{\epsilon+2}{\epsilon-1}\mathbf{Q}^b; \tag{7.6b}$$

[9] See reference 8, pp. 97–107.

and terms propagating with $c(\epsilon_S)^{-1/2}$

$$\mathbf{Q}^a=\frac{4\pi}{3}\frac{\epsilon_S+2}{\epsilon_S-1}[N\alpha\mathbf{Q}^a(r)+\mathbf{F}(r)]$$

$$+\frac{4\pi}{\epsilon_S-1}\left(\frac{c}{\omega}\right)^2\nabla[\nabla\cdot(N\alpha\mathbf{Q}^a(r)+F(r))]. \quad (7.6c)$$

Equation (7.6b) gives the usual solution to the homogeneous equation for the linear medium.

$$(4\pi/3)N\alpha=(\epsilon-1)/(\epsilon+2). \quad (7.7)$$

Equation (7.6c) is the solution to the inhomogeneous equation. It can be shown that $\mathbf{Q}^a$ is equivalent to the local fields associated with the inhomogeneous part of Eq. (2.5). This is most easily demonstrated by considering two separate cases, $\mathbf{F}$ parallel to $\mathbf{k}_S$ and $\mathbf{F}$ perpendicular to $\mathbf{k}_S$. In the parallel case Eq. (7.6c) reduces to

$$\mathbf{Q}^a=-\frac{8\pi}{9}\frac{\epsilon+2}{\epsilon}\mathbf{F}.$$

The inhomogeneous part of Eq. (7.4) can be written in terms of the linear and nonlinear polarization and the effective nonlinear source term, defined by ABDP,

$$\mathbf{P}^{\mathrm{L}}+\mathbf{P}^{\mathrm{NL}}=N\alpha\mathbf{Q}^a+\mathbf{F}=(\epsilon+2)(3\epsilon)^{-1}\mathbf{F}=\mathbf{P}^{\mathrm{NLS}}/\epsilon. \quad (7.8)$$

This is in agreement with the macroscopic definition of P^{NLS} for the longitudinal case, when D should vanish,

$$D=E+4\pi P^{\mathrm{L}}+4\pi P^{\mathrm{NL}}=\epsilon E+4\pi P^{\mathrm{NLS}}=0. \quad (7.9)$$

Similar agreement is found for the transverse component.

Equation (7.6a) constitutes the boundary conditions for the nonlinear medium. The amplitude of $\mathbf{Q}^b$ is uniquely determined by $\mathbf{Q}^a$, $\mathbf{F}$, and $\mathbf{Q}^i$. It is thus seen that the integral equations exactly parallel the differential equations. There is an inhomogeneous solution and a homogeneous solution. The amplitude of the latter is determined from the boundary conditions.

The reflected wave outside the medium is obtained much more easily since one can take the differential operators outside the integral

$$\mathbf{E}^R(r,t)=\nabla\times\nabla\times\int^{\Sigma}\frac{\mathbf{P}(r',t-R/c)}{R}dV'. \quad (7.10)$$

$P(r',t)$ is known from the solution of Eqs. (7.4) and (7.6). Integration of Eq. (7.10) is lengthy but straightforward and one gets agreement with the results of the simpler macroscopic equations in Sec. IV.

VIII. DISCUSSION AND CONCLUSION

The theoretical results of Secs. III–VI are applicable to many experimental situations. Harmonic generation is usually accomplished in a slab of a nonlinear crystal. The equations of Sec. VI give the harmonic intensity in the forward and backward directions. Both the general case of arbitrary thickness and mismatch of the phase velocities and the limiting case of phase matching in the thickness of the slab are treated in detail. The situation of harmonic generation inside a laser crystal is also described by those equations. Since the fundamental is now a standing wave, one has to sum over more than one inhomogeneous wave inside the crystal. In general, the phase velocities will not be matched. The harmonic intensity will be a periodic function of the spacing of the reflecting ends of the Fabry-Perot resonator. The intensity will not exceed the harmonic intensity of a thin slab of thickness $l=\omega c^{-1}(\epsilon_S{}^{1/2}-\epsilon_M{}^{1/2})$.

The sensitive dependence of harmonic generation on the degree of phase matching, $\epsilon_M-\epsilon_S$, and on the thickness d, makes it difficult to obtain a precise quantitative determination of the nonlinear susceptibility, by using Eqs. (6.7) or (6.8) and (6.17) or (6.18) and the experimentally observed harmonic generation from a slab. This difficulty can be avoided by using the reflected harmonic from a single boundary. One puts $\epsilon_T=\epsilon_M$ in the equations of Sec. VI, which corresponds to matching the index of refraction of the nonlinear slab with a linear medium. A simpler experimental solution to achieve the equivalent of the reflection off a semi-infinite medium is to make the other side of the slab diffuse and absorbing, or have it make an angle with the front surface. Alternatively, one may use a totally reflected fundamental beam, which generates harmonics in the penetration depth a few wavelengths λ thick as shown in Sec. V. In any case, one would still have to know quite accurately the intensity distribution of the incident laser beam in time and over the cross section. After one absolute calibration has been made, the nonlinearity of any specimen may be measured by comparing its reflected harmonic with the harmonic generated in a nonlinear reference standard, which is traversed by the same laser beam.

In crystals with a center of inversion symmetry the nonlinear polarization at the second harmonic frequency is created only by electric quadrupole effects as shown by Eq. (4.18). Consequently, the nonlinear polarization and also the amplitude of the second harmonic emanating from the boundary is reduced by a factor $(ia/\lambda\eta)^{-1}$, where a is a characteristic atomic dimension. The factor $\eta<1$ takes account of the fact that the electric dipole moment matrix element does not have its full strength in crystals which lack inversion symmetry. The odd part of the crystalline potential is smaller by a factor η than the symmetric part. Observations of Terhune on second harmonic generation in KDP and calcite show that $\eta\sim10^{-1}$ in KDP. All conclusions in this paper are equally valid for crystals with and without inversion symmetry. It has been suggested that the surface layers of a symmetric crystal

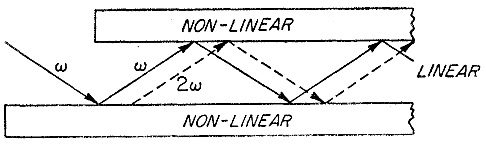

FIG. 8. Harmonic generation by multiple total reflection from a nonlinear dielectric. The dense linear medium may be a fluid contained between two nonlinear crystals or an optical fiber in a nonlinear cladding.

lack inversion symmetry, and that extra second harmonic radiation may originate from the first few atomic layers. Equations (6.12), (6.22), and (6.23) are directly applicable to such surface layers of thickness a. The magnitude of the reflected amplitude from it would be smaller by a factor η than the reflected amplitude, originating from quadrupole radiation in a boundary layer of thickness λ. It is, therefore, believed that atomic surface layers play an insignificant role in harmonic generation. In principle, their effect could be measured by observing the transmitted and reflected harmonics from slabs of varying thickness and crystallographic orientation.

The generation of harmonics in a boundary layer of the order λ, even if the fundamental wave is totally reflected, suggests a novel geometrical arrangement shown in Fig. 8. A fundamental wave at ω travels in a dense linear (fluid) medium between two nonlinear dielectric walls. Repeated total reflections occur. On each reflection second harmonic power is generated. The distance between the plates and the dispersion in the *linear* medium can be chosen such that on each reflection second harmonic radiation is generated with the correct phase to increase the harmonic intensity. Due account should be taken of the phase shifts on total reflection of fundamental and second harmonic by the methods discussed in Sec. V. The problem of phase matching is now transferred to a linear isotropic medium. If the distance between the nonlinear walls is made very small, the case of linear optical fibers with a nonlinear cladding presents itself. It is clear that the free space methods could be extended to the propagation of fundamental and harmonic waves in optical wave guides.[10]

The discussion has been restricted to plane waves and plane boundaries of infinite extent. It is possible to extend the considerations to beams of finite diameter d, to prisms, and even to curved boundaries. Some care should be exercised in extending the concept of the homogeneous and inhomogeneous wave in the nonlinear medium to rays of finite diameter. One concludes that a prism will separate these rays, as schematically shown in Fig. 9. The inhomogeneous ray leaves the prism in a direction intermediate between the fundamental ray and the homogeneous harmonic ray. One should not conclude, however, that the destructive

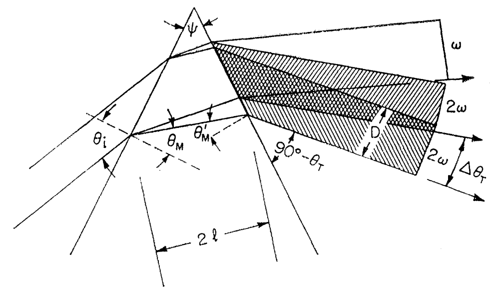

FIG. 9. The fundamental ray, the homogeneous ray, and the inhomogeneous harmonic ray are separated by a prism. The degree of phase matching and the diffraction of the rays of finite diameter limit the harmonic power in the separated beams to an amount which is equal to or less than that obtainable in a plane parallel slab.

interference which occurs between the two harmonic waves can be eliminated and that much larger harmonic power is obtainable in the separated beams. It is true that the amplitude in each beam separately is proportional to $(\epsilon_M-\epsilon_S)^{-1}$ and becomes very large as phase matching is approached. At the same time, however, the angular dispersion by the prism becomes smaller. The beams will not be separated if this dispersion is less than the diffraction angle determined by the finite diameter of the beam.

With the notation of Sec. VI and Fig. 9, one finds for the angle of deflection of the homogeneous ray in terms of the angle of incidence θ_i and the prism angle ψ,

$$\sin\theta_T=\sin\theta_i\sin\psi\cot\theta_M-\cos\psi\sin\theta_i, \tag{8.1}$$

with

$$\epsilon_M^{1/2}\sin\theta_M=\sin\theta_i. \tag{8.2}$$

Differentiation of Eqs. (8.1) and (8.2) leads to an expression of the angular deviation between the homogeneous and inhomogeneous ray in terms of the small phase velocity mismatch

$$\cos\theta_T\Delta\theta_T=\sin\theta_i\sin\psi(\epsilon_S-\epsilon_M)/(\epsilon_M\sin2\theta_M). \tag{8.3}$$

For resolution of the rays, one requires

$$\Delta\theta_T>\lambda/D, \tag{8.4}$$

where D is the diameter of the beam at the exit. The minimum length l which the center of the ray of diameter D has to travel through the prism is

$$l\geq D\sin\psi/(2\cos\theta_M\cos\theta_T). \tag{8.5}$$

Combination of Eqs. (8.3), (8.4), and (8.5) yields

$$l>\epsilon_M^{1/2}\lambda/(\epsilon_S-\epsilon_M). \tag{8.6}$$

The beam has to travel on the average at least the "coherence length" in the nonlinear prism before the homogeneous and inhomogeneous ray can be separated. This is exactly what should be expected on the basis of conservation of energy. After traversal of the coherence length, the nonlinear medium has done the maximum amount of work and created the maximum

[10] E. Snitzer, *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 348.

harmonic power. This power can then be found either in the unseparated beam transmitted in a plane parallel slab, one coherence length thick, or in separated beams after passage through a prism. A similar state of affairs applies if one tries to separate the homogeneous and inhomogeneous rays in the focal points of a chromatic lens.

The incorporation of the electromagnetic nonlinearities of matter into Maxwell's equations has led to the solution of a number of simple boundary problems. The reflection and refraction at the surfaces of nonlinear dielectrics makes it possible to analyze the generation and degeneration of light harmonics and mixing of light waves when nonlinear media occur in the optical path. This is important for the understanding of the operation of optical instruments and optical systems at very high power densities available in laser beams.

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Specific Heat of Terbium Metal between 0.37 and 4.2°K*

O. V. LOUNASMAA† AND PAT R. ROACH‡
Argonne National Laboratory, Argonne, Illinois
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The specific heat C_p of terbium metal, measured between 0.37 and 4.2°K in a He^3 cryostat, could be separated by a least squares analysis into three contributions: the lattice specific heat $C_L=0.58T^3$ (corresponding to a Debye $\theta=150$°K), the electronic specific heat $C_E=9.05T$, and the nuclear specific heat $C_N=238T^{-2}-11.9T^{-3}-4.5T^{-4}+0.38T^{-5}+0.06T^{-6}$ (C_p in mJ/mole °K). C_N is due to the splitting of the nuclear spin states by the magnetic field H_{eff} of the $4f$ electrons and by the nuclear electric quadrupole coupling. In the series expansion for C_N there are only two independent constants, the magnetic hyperfine constant a' and the quadrupole coupling constant P. Our experimental values of $a'=0.150$°K and $P=0.021$°K are in good agreement with results obtained by electron paramagnetic resonance and nuclear magnetic resonance techniques which gave $a'=0.152$°K and $P=0.029$°K. By assuming $\mu=1.52$ nuclear Bohr magnetons for Tb^{159} one obtains $H_{\text{eff}}=4.1$ MG. In sharp contrast with earlier results, our measurements revealed no anomalies in C_p between 1 and 4°K. Such anomalies thus were probably caused by impurities in the samples of the other investigators.

I. INTRODUCTION

BELOW 1°K the specific heat of terbium shows a large rise due to the magnetic hyperfine interaction between the $4f$ electrons and the magnetic moment of the nucleus. In addition to this, Bleaney and Hill[1] and Bleaney[2] have shown that the effect of nuclear electric quadrupole coupling might be of importance in calculating the nuclear specific heat of some rare earths, including terbium. The first heat capacity measurements on terbium in the liquid-helium range were performed by Kurti and Safrata[3] between 0.5 and 6°K. Recently, Heltemes and Swenson[4] have used a magnetic refrigerator cryostat to measure the heat capacity between 0.25 and 1°K. Both results are in reasonably good agreement and show the very large increase in specific heat below 1°K.

In order to determine experimentally from heat capacity measurements whether a quadrupole interaction is present, it is necessary to have accurate data at as low temperatures as possible. Bleaney and Hill[1] have analyzed the results of Heltemes and Swenson[4] and found support for the presence of a quadrupole interaction, but, because of scatter of the experimental points and possible systematic error of 10% at the lowest temperatures, this was somewhat inconclusive. It was for this reason that we decided to measure the specific heat of terbium below 1°K.

Above 1°K, the experimental points of Kurti and Safrata[3] showed considerable scatter and an apparent broad anomaly in the heat capacity between 1 and 4°K. Later measurements by Stanton, Jennings, and Spedding[5] between 1.4 and 4°K and by Bailey[6] between 1.7 and 4°K revealed a λ-type anomaly in the specific heat at about 2.3°K, but the two results did not agree with each other nor with the data of Kurti and Safrata. Differences of more than 100% were observed at 4°K. In view of this confusion, we continued our measurements up to 4°K.

The nuclei of many rare earths find themselves in a

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† Present address: Wihuri Physical Laboratory, University of Turku, Turku, Finland.

‡ Present address: University of Chicago, Chicago, Illinois.

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