Optical Harmonics and Nonlinear Phenomena*

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PREFACE

IT is the intent of many review articles to provide a scholarly presentation of a particular subject, or to furnish a meaningful collection of data and references. Such papers are often most constructive when the topic has achieved a certain maturity, or at least when the implications and objectives of the physics have been effectively established.

The purpose of the present paper, however, is necessarily of a different kind. The first observations of optical-harmonic generation have been recent, and the implications of this and related phenomena for solid-state and atomic physics are hardly established. On the one hand, it is entirely possible that most of the interesting experiments and conjectures have already been developed, or, on the other, that the general area of nonlinear optical phenomena has been probed only superficially.

It is our intent in the present paper to provide a review of most of the salient experimental accomplishments, some theoretical discussions with elegance subordinate to clarity, and a bibliography that is nominally complete to August 1962. The article has been designed with the awareness that many readers may be unfamiliar with the subject, so that descriptive and schematic presentations of most topics are included. It is hoped the paper will permit the devotee to skip various sections without loss of continuity or confusion with notation.

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I. INTRODUCTION

The development of lasers (optical masers) has made possible the production of monochromatic light beams of exceedingly high intensity. For example, the pulsed ruby laser ($\sim$6940 Å) can provide an optical flux of many kW/cm^2 in unfocused beams and many MW/cm^2 in the focal planes of simple optical systems. These intensities make the feasibility of exploiting the small but inevitable optical nonlinearities of materials most appealing. In this introductory section, we give a qualitative discussion of some theoretical and experimental matters relevant to the production of optical harmonics.

A suitable material for the production of optical harmonics must be relatively transparent to the fundamental optical frequency and the desired harmonics. In addition, there are some important crystal-symmetry considerations which affect the choice of suitable materials, particularly in the production of even harmonics. In order to develop these ideas in a simple form it will be convenient to consider a schematic expression for the dependence of the optical polarization P as a function of applied optical electric field E:

$$P = \chi E(1 + a_1 E + a_2 E^2 + \cdots) . \qquad (I.1)$$

The coefficient χ is the normal linear optical polarizability, of order unity, and the a_i are the nonlinear coefficients. A discussion of the magnitudes of the a_i is deferred to later sections; suffice it to say here they are so small that only laser light sources have sufficient intensity to provide a readily detectable production of optical harmonics.

Whereas it is most important for later discussions to recognize that the precise relationship between P and E is of tensor form, it is sufficient for the present section to deal with the scalar form of Eq. (I.1). In particular, let us consider the second term $\chi a_1 E^2$ which gives rise to the second harmonic. If the applied optical electric field is $E = E_0 \sin \omega t$, then this

quadratic term provides a contribution p to the polarization in the crystal

$$p = \mathrm{X}a_1E_0^2 \sin^2 \omega t = \mathrm{X}a_1(E_0^2/2)(1 - \cos 2\omega t) . \quad \text{(I.2)}$$

Attention is called to the unit term within the bracket. This corresponds to dc polarization within the crystal which arises from the quadratic nonlinearity in much the same way as dc currents are produced in the square-law detectors of radiofrequency practice. Attempts to observe this polarization are discussed in Sec. V.4, and theoretical discussions are presented in Secs. IV.1 and IV.3.

That part of the polarization with a cos $2\omega t$ dependence is responsible for the radiation of second harmonic from the crystal. One of the simplest experimental arrangements for producing and detecting this second-harmonic radiation is to focus the beam of a ruby laser onto the surface of a suitable crystal such as quartz. The light emerging from the crystal will be found to contain a detectable amount of the second-harmonic radiation at 3500 Å as well as the enormous amount of incident laser radiation at 7000 Å. This radiation can be detected either with spectrographic techniques or filtered photomultipliers. (Details of this and other experimental arrangements will be discussed in Sec. V.) As much as one part in 10^6 of the laser power at ~7000 Å has been converted to second harmonic in these relatively simple experiments; the actual conversion efficiency is dependent upon the particular crystal, the role of the refractive indices in the harmonic radiation process, and, of course, the intensity of the fundamental radiation.

There does exist a most important symmetry consideration which precludes *significant*, even harmonic production by those materials which are either isotropic, such as glasses, or possess a center of inversion such as calcite. (In these cases there are still higher-order processes which yield a very weak production of second harmonics, as discussed in Secs. II.2 and V.6.) When isotropy or a center of inversion is present, the polarization must reverse sign for a reversal of the applied electric field, regardless of the complexity of the tensor relationship between **E** and **P**. In order to comply with this restriction, the terms containing even powers of E in the admittedly schematic representation of Eq. (I.1) must vanish.

A pictorial demonstration of the symmetry restriction is also indicated in Fig. 1. In Fig. 1(a) is sketched the polarization dependence of a material such as calcite which possesses a center of inversion. The curve is not intended to be literal. However, the one feature that follows from the symmetry property is that a power expansion of P about $E = 0$ cannot contain even terms. If we now consider crystals which do not have a center of inversion, such as quartz, then it is possible to have the sort of polarization dependence shown in Fig. 1(b). The feature of interest here, namely the possibility of having even terms in the expansion of P around $E = 0$, has been deliberately exaggerated in the figure.

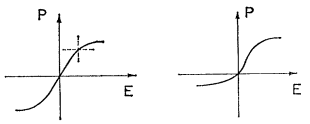

FIG. 1. Schematic illustrations of the dependence of polarization on the applied optical-electric field. (a) is appropriate to crystals such as calcite which have a center of inversion, whereas (b) applies to crystals such as quartz which lack a center of inversion. The non-linearities in both figures are exaggerated.

The lack of a center of inversion which permits second-harmonic production is identically that condition which permits piezoelectricity. However, this is not to say that the crystals most effective for harmonic production are those with the largest piezoelectric coefficients. Piezoelectricity involves ionic displacements whereas optical-harmonic generation is of primarily electronic origin.

A crystal, whose point symmetry precludes even harmonic production, can nevertheless be forced to produce the effect upon the application of a strong external dc electric field. This external bias field "slides" the origin of Fig. 1(a) over into a region, where an expansion of P about the new origin (dotted axes) now contains some even terms. (This induced effect has been observed and is discussed in Sec. V.6.) For the qualitative aspects of even-harmonic generation one may usefully regard piezoelectric crystals as containing a strong, but internal, electric bias field. It is this field which in some sense gives a preferred direction in the crystal and hence allows both piezoelectricity and the generation of even harmonics.

II. SYMMETRY RESTRICTIONS

II.1. Second-Harmonic Production

The generation of a polarization $\mathbf{p}^{2\omega}$ cos $2\omega t$ in a nonlinear medium by an optical electric field $\mathbf{E}^{\omega}$ sin ωt may be represented by a restatement of Eq. (I.2) in tensor form:[1]

$$p_i^{2\omega} = \mathrm{X}_{ijk}^{2\omega}E_j^{\omega}E_k^{\omega} . \quad \text{(II.1)}$$

[1] Here and subsequently, the convention of summation over repeated indices is adopted.

Here and in what follows, the subscripts denote Cartesian components, and the superscripts serve to indicate the relevant frequencies. $\mathbf{X}^{2\omega}$ is a $(3 \times 3 \times 3)$ third-rank tensor, which characterizes the process and whose elements $X^{2\omega}_{ijk}$ are restricted by the symmetry of the nonlinear medium.

Consider a particular physical situation described by Eq. (II.1). The medium, applied electric fields, and the polarization remain fixed in space and can now be described in a new coordinate frame. The new axes are related to the old by the transformation $\mathbf{a}$ which can be written as a (3×3) matrix representing an arbitrary combination of rotation and inversion. The vectors and tensors in the new frame (primed symbols) are

$$p'^{2\omega}_{\alpha} = a_{\alpha i} p^{2\omega}_{i} , \tag{II.2a}$$

$$E'^{\omega}_{\beta} = a_{\beta j} E^{\omega}_{j} , \tag{II.2b}$$

$$X'^{2\omega}_{\alpha\beta\gamma} = a_{\alpha i} a_{\beta j} a_{\gamma k} X^{2\omega}_{ijk} . \tag{II.2c}$$

If $\mathbf{a}$ is now restricted to be a symmetry transformation $\mathbf{A}$, then all the properties of the material are identically described in both coordinate frames. In particular, the elements of the tensor $\mathbf{X}^{2\omega}$ are the same in both coordinate frames so that

$$X^{2\omega}_{\alpha\beta\gamma} = A_{\alpha i} A_{\beta j} A_{\gamma k} X^{2\omega}_{ijk} . \tag{II.3}$$

There are thirty-two classes of crystals, each specified by a number of point symmetry transformations $\mathbf{A}$. For a particular class, each symmetry transformation yields an equation of the form Eq. (II.3) which restricts the independence of the tensor elements $X^{2\omega}_{\alpha\beta\gamma}$.

As an example of a symmetry restriction, let $\mathbf{A}$ be the inversion transformation $A_{\alpha i} = -\delta_{\alpha i}$. Equation (II.3) yields

$$\begin{aligned} X^{2\omega}_{\alpha\beta\gamma} &= (-\delta_{\alpha i})(-\delta_{\beta j})(-\delta_{\gamma k}) X^{2\omega}_{ijk} \\ &= -X^{2\omega}_{\alpha\beta\gamma} \\ &= 0 . \end{aligned} \tag{II.4}$$

Thus for any nonlinear material exhibiting inversion symmetry, $\mathbf{X}^{2\omega}$ is identically zero, and second-harmonic generation by the process under discussion is precluded. This leaves for consideration only the twenty-one crystal classes which lack a center of inversion.

The order of writing E^{ω}_{j} and E^{ω}_{k} in Eq. (II.1) is not physically significant. This suggests a convenient, contracted form (well-known to piezoelectricians) of $X^{2\omega}_{ijk}$, in which the two symmetric suffixes j and k are replaced by a single suffix m, taking values 1 through 6, such that $X^{2\omega}_{im} \equiv X^{2\omega}_{ijk}$, $j = k$ and $X^{2\omega}_{im} \equiv X^{2\omega}_{ijk} + X^{2\omega}_{ikj}$, $j \neq k$. The relation between m and jk is

m	1	2	3	4	5	6
jk	xx	yy	zz	yz	zx	xy

It is of parenthetic interest to note that symmetry class 0 has six nonzero components of $\mathbf{X}^{2\omega}$: $X^{2\omega}_{xyz} = -X^{2\omega}_{xzy}$; $X^{2\omega}_{yxz} = -X^{2\omega}_{yzx}$; $X^{2\omega}_{zxy} = -X^{2\omega}_{zyx}$. However, the extra symmetry which permits the contraction requires that $\mathbf{X}^{2\omega}$ is zero. This class is unique in that second-harmonic generation, as well as piezoelectricity, is precluded by symmetry although there is no center of inversion.

In Table I the full and contracted forms $\mathbf{X}^{2\omega}$ $(3 \times 3 \times 3)$ and $\mathbf{X}^{2\omega}$ (6×3) are quoted for two cases of practical interest, potassium dihydrogen phosphate (KDP) and quartz. The tensors may be constructed for any crystal knowing the symmetry transformations $\mathbf{A}$ and applying Eq. (II.3), the process often becoming tedious. Fortunately, the piezoelectric effect is also described by a third-rank tensor which is symmetric in two suffixes and which is therefore of the same form as $\mathbf{X}^{2\omega}$. Consequently the nonvanishing elements of $\mathbf{X}^{2\omega}$ may be read directly from tabulations of the piezoelectric coefficients.[2] However, it

TABLE I(a). $X^{2\omega}_{ijk}$ for (a) KDP (potassium dihydrogen phosphate) symmetry V_d and (b) quartz symmetry D_3.

	j	x	y	z		y	z	x		z	x	y
	k	x	y	z		z	x	y		y	z	x
	i											
(a)	x	0	0	0		a	0	0		b	0	0
	y	0	0	0		0	b	0		0	a	0
	z	0	0	0		0	0	c		0	0	c
(b)	x	e	$-e$	0		f	0	0		$-g$	0	0
	y	0	0	0		0	g	$-e$		0	$-f$	$-e$
	z	0	0	0		0	0	h		0	0	$-h$

(b). The contracted form $X^{2\omega}_{im}$ for (a) KDP and (b) quartz. The notation conforms with that used for the piezoelectric tensor.

	m	1	2	3	4	5	6
	i						
(a)	x	0	0	0	d_{14}	0	0
	y	0	0	0	0	d_{14}	0
	z	0	0	0	0	0	d_{36}
(b)	x	d_{11}	$-d_{11}$	0	d_{14}	0	0
	y	0	0	0	0	$-d_{14}$	$-2d_{11}$
	z	0	0	0	0	0	0

[2] See, for example, W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946), 1st ed., pp. 190–192; W. L. Bond, Bell System Tech. J. 22, 1 (1943); J. L. Prather, "Atomic Energy Levels in Crystals," Nat. Bur. St. (U. S.) Monograph 19, 1–84 (1961).

TABLE II. Some contributions to the nonlinear polarization.

		Lack of inversion symmetry required	Symmetric suffixes	Antisymmetric suffixes	Date of observation
$p_i^{\omega} = \mathrm{X}'^{\omega}_{ijk}E^0_jE^{\omega}_k$	linear electro-optic effect	YES	ik		1893
$+ i\mathrm{X}''^{\omega}_{ijk}\hat{k}^{\omega}_jE^{\omega}_k$	optical activity	YES		ij	1811
$+ \mathrm{X}'^{\omega}_{ijkl}E^0_jE^0_kE^{\omega}_l$	Kerr effect and electric double refraction	NO	$(il), jk$		1875 1924
$+ \mathrm{X}''^{\omega}_{ijkl}\epsilon_{jkm}B^0_mE^{\omega}_l$	Faraday and Voigt effects	NO	(il)	jk	1845 1902
$+ \mathrm{X}'''^{\omega}_{ijkl}E^{\omega}_jE^{\omega}_kE^{\omega}_l$	intensity-dependent refractive index	NO	$(i)jkl$		Not yet observed
$+ \mathrm{X}''''^{\omega}_{ijkl}B^0_jB^0_kE^{\omega}_l$	Cotton–Mouton effect	NO	$(il), jk$		1907
$p_i^{2\omega} = \mathrm{X}^{2\omega}_{ijk}E^{\omega}_jE^{\omega}_k$	second harmonic	YES	jk		1961[a]
$+ i\mathrm{X}'^{2\omega}_{ijkl}\hat{k}^{\omega}_jE^{\omega}_kE^{\omega}_l$	magnetic dipole absorption and second-harmonic emission	NO	kl		1962[bc]
$+ \mathrm{X}''^{2\omega}_{ijkl}E^0_jE^{\omega}_kE^{\omega}_l$	electric-field-induced second harmonic	NO	kl		1962[b]
$+ \mathrm{X}^{2\omega}_{ijklm}\epsilon_{jkn}B^0_nE^{\omega}_lE^{\omega}_m$	magnetic-field-induced second harmonic	YES	lm	jk	Not yet observed
$q_{ij}^{2\omega} = \eta^{2\omega}_{ijkl}E^{\omega}_kE^{\omega}_l$	quadratic polarization	NO	kl		1962[bc]
$p_i^{3\omega} = \mathrm{X}^{3\omega}_{ijkl}E^{\omega}_jE^{\omega}_kE^{\omega}_l$	third harmonic	NO	jkl		1962[b]
$p_i^0 = \mathrm{X}^0_{ijk}E^{\omega}_jE^{\omega}_k$	dc effect	YES	jk		Not yet observed

[a] (F61). [b] (T62). [c] Two effects observed but not distinguished from each other. See text.

should be stressed again that the *magnitudes* of the piezoelectric and second-harmonic tensors are not related.

II.2. Higher-Order Effects

Equation (II.1) is not a complete description of possible nonlinear optical effects. Additional terms of potential and real interest can be constructed and are summarized in Table II. The rest of this section is devoted to explanatory remarks about the construction of the table and the symmetry of the nonlinear susceptibilities.

Terms have been constructed by including dc electric and magnetic fields and optical fields restricted for simplicity to a single frequency. The unit propagation vector $\hat{k}^{\omega}$ is chosen in addition to the electric field amplitude $\mathbf{E}^{\omega}$, when a full description of the optical field is required.

A guide to the relative importance of terms in the absence of experimental data would be that the more complicated the term, the smaller must be the elements of its characteristic tensor. Adding an extra factor of an electric field reduces the resulting polarization by $\sim E/E_{\text{atomic}}$ (see Sec. IV.1) which is numerically $\sim 10^{-5}$ for 100 kV/cm (optical or dc) electric fields. By a similar argument, including a magnetic field reduces the polarization by a factor of $\sim 10^{-6}$ for a field of 10 kG.

The quadratic polarization q_{ij} includes both magnetic-dipole and electric-quadrupole contributions. Its order of magnitude is the corresponding dipole polarization multiplied by an atomic length a_0. The radiation by the quadratic polarization is out of phase with the dipole radiation and the ratio of radiated energy is reduced by a factor k^2, so that (quadratic radiation)/(dipole radiation) $\sim (q^2k^2)/p^2 \sim (a_0k)^2 \sim 10^{-6}$ evaluated for ruby laser radiation.

The factor $\hat{k}^{\omega}$ in the term $p_i^{2\omega} = i\,\mathrm{X}'^{2\omega}_{ijk}\,\hat{k}^{\omega}\,E^{\omega}_kE^{\omega}_l$ arises from the small terms in the spatial expansion of the electric field

$$\mathrm{E}(\mathbf{r}) = \mathrm{E}(0) + \mathbf{r}\cdot\nabla\mathrm{E}\cdots,$$

where

$$\mathrm{E}(\mathbf{r}) = \mathrm{E}(0)e^{i\mathbf{k}\cdot\mathbf{r}}$$

so that $\mathbf{E}(r) = \mathbf{E}(0) + i(\mathbf{k}\cdot\mathbf{r})\ \mathbf{E}_0\cdots$.

The ratio of the second term in this expansion to the first is of order ka_0. This process is similar to the quadratic polarization term $q_{ij}^{2\omega}$ in that the resulting second-harmonic radiation has the same phase and the same order of magnitude. One or both of these effects have been observed (see Sec. V.6), but it was not possible to distinguish between them experimentally.

The terms in Table II have been constructed, so that the nonlinear susceptibilities X and η are proper tensors. (To make this possible, a single-magnetic field appears accompanied by the permutation tensor ϵ_{jkm} which transforms the pseudovector to a proper second-rank tensor.) The first symmetry restriction on the susceptibilities is that of Eq. (II.3) expressed in a form suitable to the rank of the particular tensor

$$\mathrm{X}_{\alpha\beta\gamma\rho}\cdots = A_{\alpha i}A_{\beta j}A_{\gamma k}A_{\rho l}\cdots\mathrm{X}_{ijkl}\cdots\ ,$$

where $\mathbf{A}$ represents in turn each of the symmetry transformations for the nonlinear medium considered. In this way the form of the tensor of each rank for each crystal class may be determined. In particular, by an extension of Eq. (II.4) it follows that for crystals with a center of symmetry all tensors of odd rank are zero. This is not true for tensors of even rank, so that effects associated with such tensors can be present in an isotropic medium.

Tensors are symmetric in pairs of suffixes which refer to physically indistinguishable fields as stated in the last section for the case of the second-harmonic tensor $\mathbf{X}^{2\omega}$. This condition is, of course, relaxed, if the frequencies of the two fields are allowed to become different; for example, as second-harmonic production becomes "sum-frequency production." The extent of the deviation from this symmetry may be estimated from a quantum mechanical treatment (see, for example, Sec. IV).

Some pairs of suffixes are presented in Table II as being symmetric but have been written in parentheses. These are suffixes referring to p_i^{ω} and E_l^{ω}, and they are symmetric in the presence of slight absorption and dispersion to the same good approximation as are the suffixes of the usual linear optical susceptibility tensor X_{ij}^{ω}.

II.3. Kleinman's Conjecture

Kleinman has suggested (Kl 62a) that an additional symmetry condition for second-harmonic generation may be operative in materials, which are transparent to the fundamental and second-harmonic frequencies. In the notation of Eq. (II.1), the suggestion is that $\mathrm{X}_{ijk}^{2\omega} = \mathrm{X}_{jik}^{2\omega}$. This condition reduces the number of independent elements and, in some cases such as quartz, actually requires null values for particular elements. In this section we review an essentially thermodynamic argument for the conjecture prior to the more quantitative discussion of Sec. IV.2.

Let us consider those materials for which the quantity $\mathbf{P}\cdot d\mathbf{E}$ is a perfect differential or, equivalently, for which $\mathbf{P}\cdot d\mathbf{E}$ represents the electric contribution to the free energy. The perfect differential condition implies directly that the curl of $\mathbf{P}$ in $\mathbf{E}$ space is zero:

$$\frac{\partial P_x}{\partial E_y} = \frac{\partial P_y}{\partial E_x};\frac{\partial P_y}{\partial E_z} = \frac{\partial P_z}{\partial E_y};\frac{\partial P_z}{\partial E_x} = \frac{\partial P_x}{\partial E_z}. \quad \text{(II.5)}$$

For the second-harmonic polarization tensor Eq. (II.5) immediately yields the required result $\mathrm{X}_{ijk}^{2\omega} = \mathrm{X}_{jik}^{2\omega}$. Equation (II.5) could also be applied to the other contributions to P listed in Table II to obtain very useful and restrictive conditions on the relevant tensor elements.

We must now examine the validity of the surmise that $\mathbf{P}\cdot d\mathbf{E}$ is indeed a perfect differential. It is clearly not true for those materials which exhibit absorption at any of the relevant optical frequencies, since for this case $\oint \mathbf{P}\cdot d\mathbf{E} \neq 0$. Fortunately, most of the interesting materials in which second-harmonic generation has been studied are extremely transparent to the fundamental and harmonic frequencies. What damages the surmise for these materials is the presence of dispersion which destroys the single-valued character of the functional relationship between $\mathbf{P}$ and $\mathbf{E}$, so that a knowledge of the instantaneous value of $\mathbf{E}$ is no longer sufficient to determine the free energy.

The dispersion in typical crystals used for harmonic production with ruby laser radiation is only a few percent. However, the quantum-mechanical discussion of Sec. IV.2 indicates that even a few percent dispersion can seriously damage the validity of Kleinman's conjecture.

The thermodynamic argument discussed in this section is that customarily used for arguing the symmetry of the linear optical susceptibility tensor X_{ij}^{ω}. For this special situation, however, dispersion is not relevant, since the vectors related by X_{ij}^{ω} have the same time dependence. Of course, absorption is just as lethal to the symmetry of X_{ij}^{ω} as to the more general tensors discussed above.

III. THE PROPAGATION PROBLEM

III.1. Propagation of Second Harmonic in a Dispersive Medium

We now wish to examine the important restriction imposed on the radiation of harmonics by the optical dispersion of the crystal. If the refractive indices for the fundamental and second-harmonic radiation were identical, then an appreciable conversion could be achieved simply by using a thick-enough crystal. The fact that these two indices are generally different provides an important limitation on the production of second-harmonic radiation from a given crystal and geometry of illumination.

In order to exhibit the salient features of this problem, let us consider the ideal case of a plane wave of the fundamental radiation transmitted through an infinite sheet of piezoelectric material of thickness l. (Fig. 2). The amplitude of the polarization at frequency 2ω is denoted by $p^{2\omega}$, and we seek an expression for the intensity of the radiation at the exit surface of the sheet. This model does not include anisotropic effects, nor the effect of an attenuated fundamental wave, and the use of an infinite sheet excludes the need to consider edge effects. This model, however, does correspond very closely to the situation encountered in several experiments.

The electric field in the crystal at the fundamental frequency is $E_0 \sin(k_1 x - \omega t)$ and the polarization $p^{2\omega}$ which goes as 2ω will then be

$$p^{2\omega} \propto \sin(2k_1 x - 2\omega t) . \qquad \text{(III.1)}$$

It is important to note that the second-harmonic polarization is *anchored* to the spatial dependence of the fundamental wave; that is, the space part of Eq.

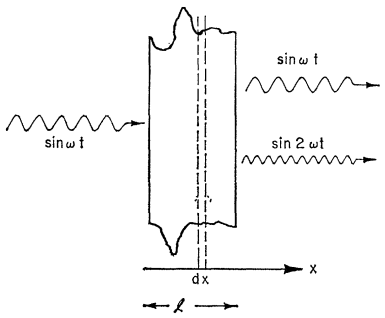

FIG. 2. Second-harmonic radiation from an infinite plane slab.

(III.1) goes as $\sin 2k_1 x$ rather than $\sin k_2 x$, where k_2 is the wave vector for second-harmonic *radiation* within the crystal. The harmonic-electric field $dE^{2\omega}$ at the exit surface of the crystal due to the harmonic polarization of a slab dx in the crystal is given by

$$dE^{2\omega} \propto dx \sin[2k_1 x - 2\omega(t - t')] , \qquad \text{(III.2)}$$

where t' is the time it takes the harmonic radiation to propagate through the crystal to the exit face and is given by

$$t' = (l - x)/v^{2\omega} = (l - x)(k_2/2\omega) . \qquad \text{(III.3)}$$

In this expression $v^{2\omega} = 2\omega/k_2$ is the phase velocity of the second-harmonic radiation in the crystal.

The total harmonic electric field at the exit surface of the crystal is

$$\int_0^l dE^{2\omega} \propto \frac{1}{2k_1 - k_2} \sin \tfrac{1}{2} l(2k_1 - k_2) \times \sin(lk_1 + lk_2 - 2\omega t) , \qquad \text{(III.4)}$$

and, therefore, the intensity $I^{2\omega}$ of the second-harmonic radiation at the exit surface of the crystal is given by

$$I^{2\omega} \propto \frac{\sin^2 \tfrac{1}{2} l(2k_1 - k_2)}{(2k_1 - k_2)^2} \propto \frac{\sin^2[(l\omega/c)(n_1 - n_2)]}{(n_1 - n_2)^2} . \qquad \text{(III.5)}$$

This equation exhibits very explicitly the potentially disastrous role played by dispersion. If $n_1 = n_2$, then the intensity at the exit face of the crystal increases directly as the square of the thickness l. However, if there is dispersion then the maximum possible intensity is that which can be obtained with a crystal of characteristic thickness l', or odd integral multiples thereof:

$$l' = \tfrac{1}{4} \lambda/(n_1 - n_2) , \qquad \text{(III.6)}$$

where λ is the free-space wavelength at the fundamental frequency. This thickness is often referred to as a "coherence length" and amounts to the order of twenty wavelengths or so for typical crystals investigated with ruby-laser radiation.

The periodic variation with respect to thickness of the intensity of the second harmonic was first verified in the elegant experiment of Maker *et al.* (M62) with crystalline quartz. They projected a parallel ruby-laser beam through a thin plate of quartz and observed the production of the second harmonic as a function of the angle between the plate normal and the laser beam. The results are given in Fig. 3, taken from their paper, and the relevant experimental parameters are listed in the caption. This experiment not only demonstrates the dispersion effects of Eq. (III.5) in a dramatic way but also provides the most useful method known today of obtaining quantitative

measurements of the tensor elements describing the second-harmonic polarization. This is because the plane wave radiation problem from a flat plate can be accurately evaluated, whereas the situation with other geometries is exceedingly difficult and requires very precise information about the optical properties of the laser beam.

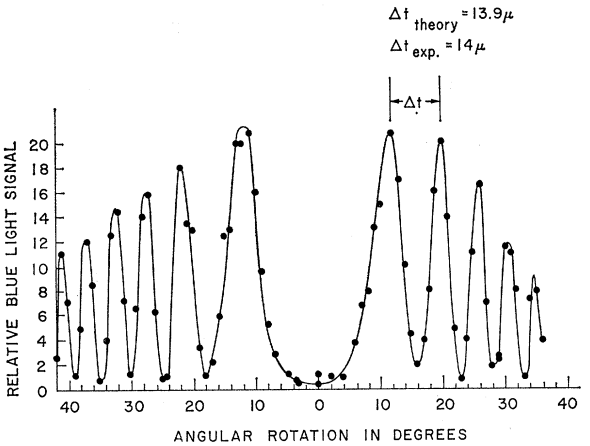

FIG. 3. Second-harmonic generation vs inclination of 0.0308-in.-thick quartz platelet to laser beam. Rotation axis normal to beam, parallel to crystal z axis. Laser beam unfocused and polarized parallel to the x axis. [Figure reproduced from reference (M62).]

The general problem of second-harmonic radiation from crystals has been studied in some detail by Bloembergen and Pershan (BP62) and by Kleinman (Kl 62b) who give quantitative expressions for some cases of practical interest. In particular, they provide most useful formulations for several embodiments of the index-matching procedures to be discussed in the next section.

III.2. Index-Matching Techniques

It has been shown in the previous section that efficient radiation of the second-harmonic requires that $k_2 = 2k_1$ or $n_2 = n_1$. This condition of matched indices is not satisfied for an isotropic crystal unless, of course, impurity absorption bands are fortuitously distributed with respect to ω or 2ω; it is not surprising that this approach has been neglected.

An ingenious method of index matching has been independently developed by Giordmaine (G62) and Maker *et al.* (M62). They exploited the fact that in certain anisotropic crystals it is possible to choose a direction of propagation such that the ordinary refractive index at one frequency is equal to the extraordinary refractive index for the other. Figure 4 shows a schematic representation of sections of four refractive index surfaces for each of two uniaxial crystals, quartz (ignoring optical activity) and KDP. The subscripts 1 and 2 on n refer to the ruby-laser fundamental and second-harmonic frequencies respectively, and superscripts o and e refer to the ordinary ray (independent of angle θ) and the extraordinary ray (a function of angle θ). As the crystals are uniaxial, the complete surfaces are generated by rotating the given sections around the z axis.

The salient feature of Fig. 4 is that for quartz neither the n_1^0 nor the n_1^e surface intersects either the n_2^0 or n_2^e surface, whereas in KDP the matching condition can be satisfied, because $n_1^0 = n_2^e(\theta_0)$ for propagation vectors making an angle θ_0 with the z axis and whose projection on the xy plane makes any angle with the x axis. $n_2^e(\theta)$ may be expressed in terms of the extraordinary refractive index for propagation at 2ω in the xy plane $n_2^e(\frac{1}{2}\pi)$ by the equation

$$\frac{1}{[n_2^e(\theta)]^2} = \frac{1}{[n_2^0]^2}\cos^2\theta + \frac{1}{[n_2^e(\frac{1}{2}\pi)]^2}\sin^2\theta\,,$$

from which one can evaluate the index matching angle θ_0 in terms of n_1^0, n_2^0, $n_2^0(\frac{1}{2}\pi)$. Giordmaine (G62) and Maker *et al.* (M62) demonstrated an increase of several orders of magnitude in second-harmonic generation near the predicted angle $\theta_0 \simeq 50°$.

The simple index-matching condition $n_1 = n_2$ may be readily generalized to the situation of 2 or more "input" waves with propagation vectors $\mathbf{k}_1, \mathbf{k}_1', \cdots$, not necessarily colinear or of the same magnitude. In order to produce an efficient radiation at some "output" frequency $\omega_2 = \omega_1 \pm \omega_1' \pm \cdots$, it is necessary that $\mathbf{k}_2 = \mathbf{k}_1 \pm \mathbf{k}_1' \pm \cdots$. This general condition has been exploited in successful experiments on third-harmonic generation (T62) and optical mixing (S62) which are described in Secs. V.3 and V.6.

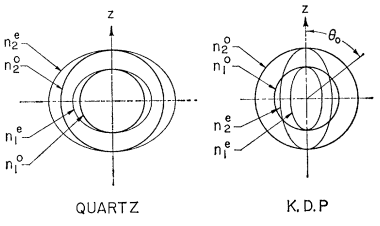

FIG. 4. Refractive index surfaces for quartz and KDP. The subscripts 1 and 2 refer to radiation at the ruby-laser frequency and the second harmonic, respectively. The superscripts o and e refer to the ordinary and extraordinary rays, respectively. The figures are exaggerated for purposes of illustration.

Another approach to the index-matching problem

was recently demonstrated,[3] in which very thin plates of x-cut crystalline quartz were stacked with their z axes alternating in direction by 180°. This effectively reverses the direction of the second-harmonic polarization in alternate plates which permits the integral of Eq. (III.4) to achieve appreciable values. In the experiment plates of quartz $\sim$0.025 cm thick were used and it was found that approximately four times as much second-harmonic radiation could be produced from two plates as one, a sixteenfold increase from four stacked plates, and so on. Although all the plates were of the same thickness, they were not exactly an odd integral multiple of the coherence length, so that the stack normal had to be oriented about 24° to the laser beam, in order to achieve the proper effective thickness for each plate. In the performance of this particular experiment, the efficiency of the method began to drop very quickly as more plates were stacked due to reflection losses at each interface. The method has a general advantage over index matching with ordinary and extraordinary rays in that the angular sensitivity is not as dramatic. It has the disadvantage that a good part of the material is "wasted," since the slabs each have a thickness of twenty or so coherence lengths due to the practical requirements of fabrication.

Armstrong *et al.* (A62) have proposed an ingenious scheme in which a periodic, relative phase shift between the fundamental radiation and the second-harmonic polarization is to be introduced by internal reflections in a quartz block. To our knowledge, the experiment has not been performed.

IV. QUANTUM MECHANICS

In this section the second-harmonic polarization is explored from the microscopic and, hence, quantum-mechanical point of view. This leads to a formalism from which, in principle, one could predict the magnitude of the second-harmonic coefficients which occur in the classical description of the earlier sections. Unfortunately, this quantitative achievement would require numerical knowledge of a plethora of matrix elements. Nevertheless, the quantum-mechanical description is most constructive for the insight it affords into the role each atom in a crystal must play in the production, and it does provide clues as to which crystals are most likely to be effective.

There have been several formulations of the problem to date. (A62, B61, H62, P62). The most extensive treatment is that of Armstrong *et al.* (A62), in which several light waves are simultaneously present in the medium, and the quantum mechanics is developed to third order in order to exhibit third-harmonic parameters. This treatment, with waves of different frequency present in the medium, permits a description of optical mixing and of situations where significant conversion occurs.

Higher-order effects, including Faraday and quadrupole interactions, have been recently studied by Price[4] and by Adler.[5] This description leads to several of the higher-order terms of Table II. In the present paper we confine our attention to the lowest-order processes.

IV.1. The Strong Single-Wave Treatment

We begin with the problem of a medium exposed to one strong electric field at the fundamental frequency ω and examine the consequent polarization for those presumably small terms having a time variation at frequency 2ω and those with no time variation at all (the "dc effect"). The electric–dipole approximation (where the relevant wavelengths are assumed to be very much larger than atomic dimensions) is exploited throughout, because it makes for simplicity and is, in fact, a very good approximation. The reader is referred to Armstrong *et al.* (A62) for a more fundamental and necessarily more elaborate formulation. For pedagogic purposes, most of the algebraic manipulations are exhibited; the reader possessed of a relatively unrusted quantum mechanics may with profit skim rapidly to Eq. (IV.5).

Consider an atomic system exposed to an electric field of the form

$$\mathbf{E} = \mathbf{E}_0 \sin \omega t \,. \tag{IV.1}$$

In dipole approximation the perturbation Hamiltonian becomes

$$H' = e\mathbf{E}\cdot\mathbf{r} \,. \tag{IV.2}$$

In what follows $\phi_n e^{-i\omega_n t}$ will be the unperturbed wavefunctions of the system, assumed real without loss of generality, and the subscript g will denote the ground state. Under the influence of the time-dependent perturbation Eq. (IV.2) the new ground-state wavefunction ψ for the system will be

$$\psi = \sum_n (\delta_{ng} + a_n^{(1)} + a_n^{(2)})\phi_n e^{-i\omega_n t} \,, \tag{IV.3}$$

where $a_n^{(1)}$ and $a_n^{(2)}$ denote the time-dependent ex-

[3] P. A. Franken, A. E. Hill, C. W. Peters (to be published). This method has also been independently proposed by Armstrong *et al.* (A62).

[4] P. J. Price (private communication, to be published).

[5] P. J. Price (private communication, to be published).

pansion coefficients in first and second order, respectively.

We now wish to examine the time dependence of the expectation value of the polarization operator for this perturbed ground state $\langle\psi|e\mathbf{r}|\psi\rangle$. A large number of terms arise if the full expression Eq. (IV.3) is used, since the expansion coefficients themselves are quite unfriendly. However, we are only concerned for the moment with those terms in $\langle\psi|e\mathbf{r}|\psi\rangle$ which contain a time dependence at 2ω and depend on E_0^2, which is the lowest power of E_0 that can develop the second harmonic. These arise from the "sandwich" of the first-order corrections with $e\mathbf{r}$, and with the similar expression involving the unperturbed ground state and those second-order corrections which carry the 2ω frequency dependence directly. Terms containing 2ω, which arise from the second-order corrections sandwiched with the second-order corrections are of order E_0^4 and, hence, to be ignored in this order of the perturbation. The explicit expressions for the expansion coefficients are given here for convenience:

$$a_n^{(1)}(t) = \frac{-e}{2i\hbar}\langle \mathrm{E}_0\cdot\mathbf{r}\rangle_{ng}\left[\frac{e^{i(\omega_{ng}+\omega)t}-1}{\omega_{ng}+\omega} - \frac{e^{i(\omega_{ng}-\omega)t}-1}{\omega_{ng}-\omega}\right],$$

$$a_n^{(2)}(t) = \frac{e^2}{4\hbar^2}\sum_m \langle \mathrm{E}_0\cdot\mathbf{r}\rangle_{nm}\langle \mathrm{E}_0\cdot\mathbf{r}\rangle_{mg}\left\{\frac{1}{\omega_{mg}+\omega}\right.$$
$$\times\left[\frac{e^{i(\omega_{ng}+2\omega)\tau}-1}{(\omega_{ng}+2\omega)} + \frac{e^{i(\omega_{nm}-\omega)\tau}}{(\omega_{nm}-\omega)} - \frac{e^{i\omega_{ng}\tau}-1}{\omega_{ng}}\right.$$
$$\left.-\frac{e^{i(\omega_{nm}+\omega)\tau}}{(\omega_{nm}+\omega)}\right] - \frac{1}{\omega_{mg}-\omega}\left[\frac{e^{i\omega_{ng}\tau}-1}{\omega_{ng}}\right.$$
$$\left.\left.-\frac{e^{i(\omega_{ng}-2\omega)\tau}-1}{(\omega_{ng}-2\omega)} - \frac{e^{i(\omega_{nm}+\omega)\tau}-1}{(\omega_{nm}+\omega)} + \frac{e^{i(\omega_{nm}-\omega)\tau}-1}{(\omega_{nm}-\omega)}\right]\right\}. \tag{IV.4}$$

In these expressions, the perturbation was assumed to be turned on at $t = 0$, and terms such as ω_{ng} denote $\omega_n - \omega_g$. Using Eqs. (IV.4) in (IV.3) to calculate that part of the expectation value of $e\mathbf{r}$ which has a 2ω time dependence, one obtains

$$\langle\psi|er|\psi\rangle_{2\omega} = \frac{-e^2}{2\hbar^2}\sum_{nn'}\langle \mathrm{E}_0\cdot\mathbf{r}\rangle_{n'g}\langle \mathrm{E}_0\cdot\mathbf{r}\rangle_{ng}\langle e\mathbf{r}\rangle_{n'n}(\cos 2\omega t)$$
$$\times\left[\frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}-\omega)}\right] - \frac{e^2}{2\hbar^2}\sum_{nn'}\langle \mathrm{E}_0\cdot\mathbf{r}\rangle_{n'g}$$
$$\times\langle \mathrm{E}_0\cdot\mathbf{r}\rangle_{n'n}\langle e\mathbf{r}\rangle_{gn}(\cos 2\omega t)$$
$$\times\left[\frac{1}{(\omega_{ng}+2\omega)(\omega_{n'g}+\omega)} + \frac{1}{(\omega_{ng}-2\omega)(\omega_{n'g}-\omega)}\right]. \tag{IV.5}$$

The symmetry restrictions discussed in Sec. II.1 for this second-harmonic process are embodied in the triple matrix element products of Eq. (IV.5). For example, the requirement that there be no inversion symmetry is apparent, because the products must each vanish if the original unperturbed ϕ_n are eigenstates of parity. An isotropic medium or one with a center of inversion is necessarily a parity-conserving system.

The first summation indicates a crystal is likely to be particularly effective in producing the second-harmonic polarization, if there exist excited states that lie near a frequency ω above the ground state. Such crystals, however, are likely to be poor choices owing to the almost certain occurrence of strong absorption in the region of the second-harmonic frequency.

If the first optical absorption band lies just above 2ω from the ground state, the second summation of Eq. (IV.5) indicates a most favorable condition. We must then try to determine just how close one can work to this absorption band, without seriously affecting the radiation of the second harmonic. One immediately notices in Eq. (IV.5) that several of the dipole matrix elements and the resonance denominators are common to the calculation of an absorption cross section. However, the 2ω polarization depends on a triple product of matrix elements, whereas the absorption coefficient goes as the square of a matrix element. This fact alone just about precludes the possibility of a useful calculation without an accurate *a priori* knowledge of the relevant elements. One can only point out that it is advisable, other factors being equal, to work as close to an absorption band at 2ω as is consistent with a relatively large transparency for the 2ω radiation. The experimental work of Lax *et al.* (L62) lends some support to this contention, but it is hard to grant the "other factors being equal" plea in comparing quite disparate crystals.

An expression for the dc polarization can be derived in exactly the same fashion as Eq. (IV.5). In this case the expectation value $\langle\psi|e\mathbf{r}|\psi\rangle$ is examined for those terms which have no time variation. The result is

$$\langle\psi|e\mathbf{r}|\psi\rangle_{dc} = +\frac{e^2}{4\hbar^2}\sum_{nn'}\langle \mathrm{E}_0\cdot\mathbf{r}\rangle_{n'g}\langle \mathrm{E}_0\cdot\mathbf{r}\rangle_{ng}\langle e\mathbf{r}\rangle_{n'n}$$
$$\times\left[\frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}+\omega)} + \frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}-\omega)}\right]$$
$$+\frac{e^2}{2\hbar^2}\sum_{nn'}\langle \mathrm{E}_0\cdot\mathbf{r}\rangle_{nn'}\langle \mathrm{E}_0\cdot\mathbf{r}\rangle_{n'g}\langle e\mathbf{r}\rangle_{ng}$$
$$\times\left[\frac{1}{\omega_{ng}}\left(\frac{1}{\omega_{n'g}+\omega} + \frac{1}{\omega_{n'g}-\omega}\right)\right]. \tag{IV.6}$$

If we consider the case where the nearest absorption bands are of much greater frequency than ω or

2ω, then a comparison of Eq. (IV.5) with Eq. (IV.6) shows that the amplitude of the polarization at frequency 2ω is just equal to the dc polarization. This is in agreement with the classical prediction Eq. (I.2) and is expected because the large-gap approximation should carry the quantum mechanical formulation directly to the adiabatic, or classical, limit.

It is of interest to compare the amplitude of the dc polarization with that of the polarization at frequency 2ω in the case for absorption bands near ω or 2ω. In these cases, the 2ω polarization increases as $1/\Delta\omega$, where $\Delta\omega$ is the difference between an absorption frequency ω_{ng} of the crystal and either ω or 2ω. In the case of the dc polarization, however, there is no sharp increase as the absorption band approaches 2ω. The dramatic effect occurs when the absorption band lies near ω, in which case the dc polarization increases as $1/\Delta\omega^2$. The objection noted earlier in this section to using a crystal with such an absorption band for the production of second harmonic is not operative for observing the dc effect, since the fact that the 2ω radiation will very likely be absorbed by the crystal is of no particular concern.

Finally, it is instructive to examine the quantum-mechanical expression Eq. (IV.5) and see how it can be reduced to a form resembling the classical expression given by Eq. (I.1). For simplicity let us assume there is only one excited state and that the matrix element of r is simply a_0, some characteristic atomic length, regardless of the indices. That is, $\langle \mathbf{E}_0 \cdot \mathbf{r} \rangle_{ng \text{ or } nn} = E_0 a_0$, $|\langle e\mathbf{r} \rangle|_{ng \text{ or } nn} = e a_0$, and $\hbar\omega_{ng} = e^2/a_0$. (We are treating the whole affair as scalar for this purpose.) In the limit $\omega << \omega_{ng}$, Eq. (IV.5) then becomes simply

$$p^{2\omega} = \tfrac{3}{2} a_0^3 E_0 [(a_0^2/e) E_0] . \qquad \text{(IV.7)}$$

Here, a_0^3 is simply the linear polarizability of the atom and Eq. (IV.7) is therefore identical in form to the second term in Eq. (I.1) which describes the second-harmonic polarization. The factor a_0^2/e is to be associated with a_1 in Eq. (I.1) and is nothing more than an inverse atomic electric field. This reasoning led to the original speculation (F61) that the second-harmonic coefficients should be of the order of inverse atomic fields, something like 10^{-7} in Gaussian units. The analysis of currently available data indicates that the coefficients are some three orders of magnitude smaller in practice. This is most likely due to the relevant dipole matrix elements being quite a bit smaller than indicated by the little more than dimensional reasoning given above. This minuteness occurs if the crystalline fields are not strong enough to introduce the appreciable mixing of atomic states of different parity which is required for a husky development of the matrix elements.

It is important to emphasize that the treatment of this and the following sections tacitly embraces the ionic contributions to the nonlinear polarization. The $\phi_n e^{-i\omega_n t}$ which we have used as unperturbed eigenstates do include the ionic states, insignificant though their contribution may be too many of the exclusively high-frequency phenomena. The possibility of long-range effects or cooperative phenomena between different cells are not included in the present treatment.

IV.2. Kleinman's Conjecture

In Sec. II.3 Kleinman's conjecture concerning an additional symmetry restriction on the second-harmonic coefficients was discussed from a thermodynamic point of view. We are now in a position to examine this restriction within the framework of the quantum-mechanical formulation and elicit with more precision the role played by optical dispersion.

The conjecture is that $\mathrm{X}^{2\omega}_{ijk} = \mathrm{X}^{2\omega}_{jik}$, where $\mathbf{X}^{2\omega}$ is a third-rank tensor describing the generation of the second-harmonic polarization $p^{2\omega}$

$$p_i^{2\omega} = \mathrm{X}^{2\omega}_{ijk} E_j E_k . \qquad \text{(IV.8)}$$

Keeping in mind that $\mathrm{X}^{2\omega}_{ijk} = \frac{1}{2}(\mathrm{X}^{2\omega}_{ijk} + \mathrm{X}^{2\omega}_{ikj})$, one can group the terms in the quantum-mechanical expression for the second-harmonic polarization Eq. (IV.5) in order to exhibit the tensor elements explicitly:

$$\mathrm{X}^{2\omega}_{ijk} = \frac{-e^3}{4\hbar^2} \sum_{nn'} \Big[\langle r_i \rangle_{nn'} ({}^{\mathbf{n}}\langle r_j \rangle_{n'g} \langle r_k \rangle_{ng} + \langle r_j \rangle_{ng} \langle r_k \rangle_{n'g})^{\mathbf{n}} A_{nn'} + \langle r_i \rangle_{ng} ({}^{\mathbf{n}}\langle r_j \rangle_{n'g} \langle r_k \rangle_{nn'} + \langle r_j \rangle_{nn'} \langle r_k \rangle_{n'g})^{\mathbf{n}} B_{nn'} \Big] , \qquad \text{(IV.9)}$$

where r_i denotes x, y, or z, and the frequency-dependent terms $A_{nn'}$ and $B_{nn'}$ are

$$\begin{aligned} A_{nn'} &= 1/(\omega_{n'g} + \omega)(\omega_{ng} - \omega) \\ B_{nn'} &= 1/(\omega_{ng} + 2\omega)(\omega_{n'g} + \omega) \\ &\quad + 1/(\omega_{ng} - 2\omega)(\omega_{n'g} - \omega) . \end{aligned} \qquad \text{(IV.10)}$$

In the limit of the laser frequency ω approaching zero (very much less than ω_{ng}, $\omega_{n'g}$, etc.), Eq. (IV.10) reduces to

$$\lim_{\omega \to 0} |B_{nn'} = B_{n'n} = 2A_{nn'} = 2A_{n'n} = 2/\omega_{ng}\omega_{n'g} . \qquad \text{(IV.11)}$$

Under this circumstance a few minutes' inspection of Eq. (IV.9) reveals the validity of Kleinman's conjecture, that is

$$\lim_{\omega \to 0} |\mathrm{X}_{ijk} = \mathrm{X}_{jik} . \qquad \text{(IV.12)}$$

This is an expected result because the limit of low laser frequency corresponds in the present model to the classical, or adiabatic, condition, where all effects due to dispersion or absorption should be negligible. It is exactly in this region of the spectrum that the thermodynamic argument of Sec. II.3 has a strong *a priori* claim to validity.

The situation where the laser frequency is small, but not entirely negligible compared with ω_{ng}, $\omega_{n'g}$, etc., is the one of practical interest for most substances being currently investigated. Under these conditions, Eq. (IV.9) becomes quite intractable. However, we can gain some insight into the pathology of $\mathbf{X}^{2\omega}$, by introducing a dimensionless frequency parameter $\epsilon_{nn'}$, which is a measure of how seriously the limiting equality of Eq. (IV.11) is violated:

$$B_{nn'}/2A_{nn'} = 1 + \epsilon_{nn'},$$
$$\epsilon_{nn'} = [(\omega_n - \omega)(2\omega^2 + \omega_n\omega_{n'})/(\omega_n^2 - 4\omega^2)(\omega_{n'} - \omega)] - 1. \tag{IV.13}$$

Defined in this way, $\epsilon_{nn'}$ can give a crude measure of the validity of Kleinman's conjecture for a given crystal:

$$|\mathbf{X}_{ijk} - \mathbf{X}_{jik}| \approx \bar{\epsilon}\mathbf{X}_{ijk}, \tag{IV.14}$$

where $\bar{\epsilon}$ is the average value of $\epsilon_{nn'}$. It is instructive to evaluate $\bar{\epsilon}$ for the case of quartz, where the energy gap and, hence, ω_{ng}, $\omega_{n'g}$, etc., is roughly five times the ruby laser frequency. We find that $\bar{\epsilon} \approx 0.3$. This result indicates, for example, that the d_{14} term in quartz [Table I(b)] is not necessarily zero, as required by the Kleinman conjecture, but that it could be of the order of 1/3 as large as the d_{11} term. Similarly in KDP [Table I(b)] the d_{14} and d_{36} terms need not be equal but could differ by the order of 30%. For crystals with absorption edges nearer the laser frequency than quartz or KDP the validity of the conjecture is damaged even more.

The fact that the relatively small ($\sim$2%) dispersion in quartz between the laser frequency and the second harmonic can lead to such a large disparity in Kleinman's conjecture is actually quite reasonable. While it is true that the dispersion is only about 2%, it must be noted that this implies an $\sim$7% variation in the optical polarizability χ. ($n^2 = 1 + \chi$). Since χ depends on single energy denominators such as $1/(\omega_{ng} - \omega)$, rather than the quadratic forms of Eq. (IV.10), the relevant terms for the second-order polarizability of quartz each vary by some 15% in going from the fundamental to the second harmonic. It is this large variation which accounts for the predicted disparity in Kleinman's conjecture for these materials.

IV.3. Sum and Difference Frequencies, and the Linear Electro-Optic Effect

It is now instructive to examine the situation, where two laser beams with frequencies ω_1 and ω_2 are present in the medium. In particular, we seek those terms in the expectation value of the polarization $\langle\psi|e\mathbf{r}|\psi\rangle$ which exhibit a time dependence at frequencies $(\omega_1 + \omega_2)$ and also at $(\omega_1 - \omega_2)$. The calculation proceeds exactly as in Sec. IV.1 but with the complication that Eq. (IV.1) describing the electric field $\mathbf{E}$ in the medium becomes

$$\mathbf{E} = \mathbf{E}_1 \sin \omega_1 t + \mathbf{E}_2 \sin \omega_2 t. \tag{IV.15}$$

After the pursuit of tedious algebra one obtains

$$\langle\psi|e\mathbf{r}|\psi\rangle_{\omega_1+\omega_2} = \frac{-e^2}{2\hbar^2}\cos(\omega_1 + \omega_2)t\Bigg[\sum_{nn'}\langle\mathbf{E}_1\cdot\mathbf{r}\rangle_{ng}\times\langle\mathbf{E}_2\cdot\mathbf{r}\rangle_{n'g}\langle e\mathbf{r}\rangle_{nn'}\Bigg\{\frac{1}{(\omega_{n'g} - \omega_2)(\omega_{ng} + \omega_1)} + \frac{1}{(\omega_{ng} - \omega_1)(\omega_{n'g} + \omega_2)}\Bigg\} + \sum_{nn'}\langle\mathbf{E}_1\cdot\mathbf{r}\rangle_{n'g}\langle\mathbf{E}_2\cdot\mathbf{r}\rangle_{nn'}\times\langle e\mathbf{r}\rangle_{ng}\Bigg\{\frac{1}{(\omega_{n'g} + \omega_1)(\omega_{ng} + \omega_1 + \omega_2)} + \frac{1}{(\omega_{n'g} - \omega_1)(\omega_{ng} - \omega_1 - \omega_2)}\Bigg\} + \sum_{nn'}\langle\mathbf{E}_2\cdot\mathbf{r}\rangle_{n'g}\times\langle\mathbf{E}_1\cdot\mathbf{r}\rangle_{nn'}\langle e\mathbf{r}\rangle_{ng}\Bigg\{\frac{1}{(\omega_{n'g} + \omega_2)(\omega_{ng} + \omega_1 + \omega_2)} + \frac{1}{(\omega_{n'g} - \omega_2)(\omega_{n'g} - \omega_1 - \omega_2)}\Bigg\}\Bigg], \tag{IV.16a}$$

$$\langle\psi|e\mathbf{r}|\psi\rangle_{\omega_1-\omega_2} = \frac{e^2}{2\hbar^2}\cos(\omega_1 - \omega_2)t\Bigg[\sum_{nn'}\langle\mathbf{E}_1\cdot\mathbf{r}\rangle_{ng}\langle\mathbf{E}_2\cdot\mathbf{r}\rangle_{n'g}\times\langle e\mathbf{r}\rangle_{nn'}\Bigg\{\frac{1}{(\omega_{ng} + \omega_1)(\omega_{n'g} + \omega_2)} + \frac{1}{(\omega_{ng} - \omega_1)(\omega_{n'g} - \omega_2)}\Bigg\} + \sum_{nn'}\langle\mathbf{E}_1\cdot\mathbf{r}\rangle_{n'g}\times\langle\mathbf{E}_2\cdot\mathbf{r}\rangle_{n'n}\langle e\mathbf{r}\rangle_{ng}\Bigg\{\frac{1}{(\omega_{n'g} + \omega_1)(\omega_{ng} + \omega_1 - \omega_2)} + \frac{1}{(\omega_{n'g} - \omega_1)(\omega_{ng} - \omega_1 + \omega_2)}\Bigg\} + \sum_{nn'}\langle\mathbf{E}_2\cdot\mathbf{r}\rangle_{n'g}\times\langle\mathbf{E}_1\cdot\mathbf{r}\rangle_{n'n}\langle e\mathbf{r}\rangle_{ng}\Bigg\{\frac{1}{(\omega_{n'g} + \omega_2)(\omega_{ng} - \omega_1 + \omega_2)} + \frac{1}{(\omega_{n'g} - \omega_2)(\omega_{ng} + \omega_1 - \omega_2)}\Bigg\}\Bigg]. \tag{IV.16b}$$

An examination of Eq. (IV.16b) in the limit of ω_1 approaching ω_2 yields an expression identical to Eq. (IV.5) for the second harmonic. This is an entirely expected result, since the generation of a second harmonic may be considered as simply the mixing of two identical frequencies.

The intimate connection between the generation of low difference frequencies (the "dc effect") and the linear electro-optic effect was first pointed out by Armstrong *et al.* (A62) in their general three-field treatment in which index and frequency permutation relations are developed. We now wish to examine this connection in the light of the explicit expressions for the simpler two-field treatment of this section.

Eq. (IV.16b) may be conveniently expressed in tensor notation

$$p_i^{(\omega_1-\omega_2)} = \mathrm{X}_{ijk}^{(\omega_1-\omega_2)} E_j^{\omega_1} E_k^{\omega_2} . \qquad \text{(IV.17)}$$

As before, the superscripts will serve to indicate the frequencies. We now wish to examine Eq. (IV.17) in the two interesting limits of ω_2 approaching ω_1 and of ω_2 approaching zero. These limits may be written formally as

$$\omega_2 \rightarrow \omega_1 | p_i^0 = \mathrm{X}_{ijk}^0 E_j^{\omega_1} E_k^{\omega_1} \qquad \text{(IV.18a)}$$

$$\omega_2 \rightarrow 0 \ | p_i^{\omega_1} = \mathrm{X}_{ijk}^{\omega_1} E_j^{\omega_1} E_k^0 \qquad \text{(IV.18b)}$$

The situation embraced by Eq. (IV.18a) is simply that of the "dc effect," or low-frequency difference generation. Equation (IV.18b) however, describes the linear electro-optic effect,[6] in which the ordinary optical polarizability of a medium is modified by the presence of a strong electric field at "zero" frequency. That is, the term p_i^q in Eq. (IV.18b) merely represents the usually very small *change* in the optical polarization in the i direction due to a strong zero-frequency electric field. (The ordinary linear optical polarization is not included, nor is it germane of course, to the development of this and other sections of the paper.)

An explicit examination of Eq. (IV.16b) in the limits of ω_2 approaching ω_1 and zero reveals the following connection between the third-rank tensors of Eqs. (IV.18a) and (IV.18b):

$$\mathrm{X}_{ijk}^0 = \mathrm{X}_{jik}^{\omega_1} \qquad \text{(IV.19)}$$

It is entirely as if the indices, *as well as the frequencies*, were simply interchanged in Eqs. (IV.18a) and (IV.18b).[6a]

This identity of the "dc" and electro-optic tensors enables one to predict the magnitude of the induced dc polarization and the production of low-frequency radiation (up to the far infrared in many substances) produced by beating two lasers of nearly the same frequency. To date none of the experiments have revealed either dc polarizations or far infrared difference radiation, in seeming contradiction with the prediction of Eq. (IV.19) and the numerical data available for the electro-optic coefficients. These experiments and the numerical data are reviewed in Sec. V.4.

V. REVIEW OF EXPERIMENTS

V.1. General Remarks

Many of the experiments involve shining the focused or unfocused radiation from a ruby laser on suitable materials and analyzing some part of the spectrum of the transmitted light. The following remarks on experimental considerations are germane to much of this work.

The green and shorter wavelength radiation from the laser flashlamp must usually be eliminated from the primary beam in order to avoid obscuring the nonlinear phenomena under study. In most circumstances commercial, deep red glass filters of the Corning type have proved satisfactory. It must be pointed out that various filters, particularly some of the gelatin types, can exhibit bizarre effects under the influence of the extremely high radiation intensity characteristic of laser beams. For example, the transmission characteristics have been found to vary with time during the pulse (BM 62).

In most of the experiments with second harmonics, the intensity of the harmonic radiation is six or more orders of magnitude below that of the ruby-laser intensity. A good quartz-prism spectrograph and photographic detection with red insensitive plates has proved satisfactory for many of these experiments. However, this is a poor system for work in which the second-harmonic radiation is too weak to give a developable image in a reasonable number of laser pulses. More satisfactory arrangements have exploited photomultipliers in conjunction with monochromators, or just a filter cell containing saturated copper sulphate solution located in front of a photomultiplier. At 3500 Å, 1.5 inches of this solution is quite transparent and yet attenuates the ruby-laser radiation by some 18 orders of magnitude.[7]

The data acquired with filtered photomultiplier

[6] B. H. Billings, J. Opt. Soc. Am., **39**, 797, 802 (1949); R. O. B. Carpenter, *ibid.* **40**, 225 (1950). For a convenient summary of the available data see: *American Institute of Physics Handbook*, edited by D. Gray (McGraw-Hill Book Company, New York, 1957).

[6a] *Note added in proof.* This permutation symmetry relation can be derived without recourse to explicit quantum mechanical expressions. [N. Bloembergen, private communication].

[7] R. W. Terhune (private communication).

detection schemes requires far more caution in interpretation than the data achieved with a spectrograph. This is because it is possible in many experiments to generate a detectable amount of radiation in the 3000–5000 Å range by incandescent processes at those surfaces in the apparatus which are exposed to the unattenuated laser beam. The use of a good monochromator in conjunction with a filtered photomultiplier is a far more hygienic procedure.

V.2. Second-Harmonic Experiments

The generation of an optical second harmonic was first observed in experiments where a ruby laser beam was focused on the front surface of a plate of crystalline quartz (F61). The emergent radiation from the crystal was examined with a prism spectrograph to separate the second harmonic ($\sim$3470 Å) from the enormous amount of laser radiation at $\sim$6940 Å. It was estimated that $\sim 10^{19}$ incident laser photons produced $\sim 10^{11}$ second-harmonic photons, in the interval of $\sim$1 msec characteristic of the laser pulse. The expected dependence (see Table I) of the conversion efficiency on the relative orientation of the crystal axes and the laser polarization was verified.

Second-harmonic generation with unfocussed laser beams was first demonstrated by Giordmaine (G62) and Maker *et al.* (M62) in KDP and quartz. Both groups established the efficacy of the index matching scheme for KDP discussed in Sec. III.2. They also found the index-matching technique very useful in KPD and similar crystals even for the case of focused beams, provided the impinging cone of laser radiation contained the index-matching direction. In experiments by both of these groups total conversion efficiences of the order of 10^{-6} were achieved[7a] with KDP with laser pulses of a few joules in $\sim$1/2 msec.

Kleinman (K1 62b) has estimated from the available data on the results of unfocused ruby laser beams on quartz and KDP plates that d_{11} (quartz) $\cong 10^{-10}$ esu and d_{36} (KDP) $\cong 6 \times 10^{-10}$ esu (see Table I for notation). For a detailed and quantitative analysis of the radiation problem with focused and unfocused beams the reader is referred to Kleinman's paper.

Lax *et al.* (L62) have measured the second-harmonic production in quartz, strained Al_2O_3, and ZnS. The data provides fair agreement with their semiclassical theory of the process.

Savage and Miller (SM62) have compared the efficiency of second-harmonic generation in a number of crystals in a specific experimental situation. Their results are reproduced in Table III. A ruby laser was used giving an optical power of 200 W in the pulse at the focusing lens (except for crystals marked * in Table III, which would have been damaged by such an intensity.) The focusing lens was 16 mm f.l. $f/2$, and a fast ($f/4.5$) monochromator with suitable filters and photomultiplier detection was employed. The apparatus could detect a minimum of 10 second-harmonic photons per laser pulse. The variation of the second-harmonic intensity with fundamental intensity and crystal orientation was checked. A 25% variation in second-harmonic generation between different crystals of the same substance, attributable to surface irregularities, is a measure of the precision of the experiment. Two results are of particular interest. Triglycine sulphate (TGS) was found to be an order of magnitude less efficient than quartz in contrast to the observations of other groups[8] who have found TGS significantly more efficient than quartz. Recent unpublished work by Miller and Savage[9] indicates that the variation of the domain structure in TGS from sample to sample may account for this discrepancy. The other point of interest is that no observable second harmonic was generated by guanidene carbonate (D_4) which null result would follow from Kleinman's conjecture (Secs. II.3 and III.2).

TABLE III. Relative values of second-harmonic output (SM62).

Material	Number of samples	Crystal face normal to beam	Relative value
KDP	2	(110)	1000
ADP	2	(110)	720
K-doped $NaNbO_3$*[a]	2	(101)	230
Quartz	3	(001)	34.0
$NaClo_3$*[a]	2	(110)	11.0
$NaClO_3$*[a]	2	(111)	8.0
Tourmaline	1	(001)	10.0
TGS	2	(101)	3.2
TGS	2	(100)	1.3
TGS	2	(001)	1.0
Rochelle salt	3	(110)	1.2
$NaBrO_3$	2	(111)	0.54
GASeH	1	(001)	2.0
GGSH	1	(001)	0.82
GASH	3	(001)	0.39
GGSeH	1	(001)	0.21

[a] Those crystals marked with an asterisk were explored with low laser power.

Miller and Savage (MS62) have performed a similar experiment using a $CaWO_4$:Nd^{+3} laser as a

[7a] *Note added in proof.* Conversion efficiencies of about 20% have recently been achieved by Terhune, Maker and Savage (to be published). The experiments were performed with a 1 MW "giant-pulse" ruby laser focused into a plate of ADP at the index-matching angle. These authors also report conversion efficiencies for the third harmonic as high as 10^{-5}.

[8] Private communications from R. W. Terhune, H. Boyne, and our laboratory.

[9] R. C. Miller (private communication).

source. Their laser radiated at 1.0582 μ with a power of about 30 W during the pulse. The second harmonic is now 5291 Å, which allows the investigation of crystals which are opaque to the second harmonic of ruby-laser radiation. These considerations apply, for example, to CdS, ZnO, $PbTiO_3$, $BaTiO_3$, which were among the crystals investigated. However, KDP and ADP were still found to be the most efficient second-harmonic generators even at this longer wavelength. These authors have also survived visual observation of this harmonic.

Boyne and Martin (BM62) have used a 21-ft radius, 15 000 lines per in. concave grating to compare the wavelength of ruby laser light to that of the second harmonic produced in various materials. In experiments with two different ruby rods and three different crystals, the ratio was found to be two, within the experimental error imposed by the linewidth of the radiation and the resolution of the instrument. The accuracy varied with the efficiency of harmonic production and was given as: Quartz $\pm$ 6 ppm, KDP $\pm$ 3 ppm, TGS $\pm$ 4 ppm.

Abella (Ab62) has recently performed a series of experiments with ruby laser second-harmonic generation in KDP. A distinguishing feature of this work was that the laser was operated as close to threshold as possible so that effects due to thermally induced shifts of laser frequency throughout the pulse were minimized. The conclusion of this work is that the frequency ratio is two, within $\pm$ 1.5 ppm.

These careful examinations of the frequency ratio are motivated in part by the possibility that phonon processes in the second-harmonic production might be significant. These processes could in principle provide shifts as well as broadening in the observed second harmonic radiation. No evidence for these effects were found within the precision of the work of Abella, or Boyne and Martin. If and when second harmonics can be achieved with the use of extremely monochromatic sources it might be well worth extending these studies.

V.3. Sum-Frequency Experiments

The wavelength of the ruby laser radiation depends on the temperature of the ruby (AC61), with a variation of about 10Å between liquid nitrogen and room temperature. In the experiment of Bass *et al.* (B62), the light from two lasers operated at these temperature extremes were mixed in a TGS crystal. The two laser beams were combined with a half-silvered mirror and focused onto the crystal with a 16 mm f.l. lens. Spectrographic examination of the emergent radiation revealed the presence of an ultraviolet frequency equal to the sum of the two laser frequencies, as well as the second harmonics of each component. The intensity of the sum frequency was intermediate between the second harmonics, as expected, and the second harmonics as well as the sum frequency disappeared when the crystal was above its Curie temperature (50°C), for which condition TGS is known to be centrosymmetric.

Smith and Braslau (S62) have demonstrated the mixing of ruby laser radiation with both the green and yellow lines from a mercury arc lamp. Collimated beams from the sources were combined with a dichroic mirror and the combined beam passed through a KDP crystal in an index-matching direction. The sum frequencies were distinguished by a monochromator and filters and detected with a photomultiplier. The intensity at the sum frequency was shown to be proportional to the mercury lamp intensity and to have the expected dependence on orientation of the crystal. Estimates of intensities were: ruby-laser beam, 1000 W; mercury green line, 0.02 W; sum frequency, 10^{-9} W.

Miller and Savage (MS62) have observed the sum frequency of ruby and $CaWO_4$:Nd^{+3} radiations which were combined and focussed into various crystals (KDP, ADP, $BaTiO_3$, tourmaline) exploiting index matching, in the same apparatus mentioned in Sec. V.2 for second-harmonic generation. The intensities before combination were: ruby laser, 115 W; $CaWO_4$:Nd^{+3} laser, 30 W. 10^6 to 10^7 photons at the sum frequency were detected.[9a]

V.4. The dc Effect and Low Difference Frequencies

Theoretical aspects of the "dc effect" in which radiation at two slightly different frequencies produce a low-frequency polarization in the medium have been discussed in Sec. IV.3. The difference frequency is considered "low" when it is small compared with any ionic or electronic absorption bands in the crystal. The theory of Sec. IV.3 established a relationship between the "dc effect" and the linear electro-optic effect. This relationship can be expressed in terms of the contracted tensor elements X^0_{im} characteristic of the dc effect and the elements X^ω_{mi} characteristic of the electro-optic effect

$$\mathrm{X}^0_{im} = \mathrm{X}^\omega_{mi} . \tag{V.1}$$

The experimental data on the electro-optic effect[6] is conventionally expressed by a contracted tensor

[9a] *Note added in proof.* These authors have also observed the sum frequency of the 1.0582 μ and 1.0652 μ lines emitted simultaneously by the $CaWO_4$:Nd^{+3} laser, as well as the second harmonics of each.

r_{mi} defined in terms of the index of refraction n by

$$\Delta(1/n^2)_m = r_{mi}E_i^0 . \qquad (V.2)$$

Manipulation of Eqs. (IV.12), (V.1), and (V.2) yields the relation

$$X_{im}^0 = -(n^4/4\pi)r_{mi} . \qquad (V.3)$$

The relevant experimental data for quartz and KDP in units of 10^{-8} esu are [6,10]

$$\begin{aligned} \text{Quartz: } & r_{41} = 1.4 , \quad r_{11} = 0.59 , \quad X_{14}^0 = -0.63 \\ & X_{11}^0 = -0.27 , \\ \text{KDP: } & r_{63} = -32 , \quad r_{41} = 26 , \quad X_{36}^0 = 13 , \\ & X_{14}^0 = -11 . \end{aligned} \qquad (V.4)$$

Giordmaine, Richards, and Yariv[11] have searched for the dc effect in quartz in a mixing experiment with the beams from "hot" and "cold" ruby lasers (See Sec. V.3 on the mixing experiments of Bass *et al.*) The difference frequency in this case lies in the far microwave region at a wavelength of 0.05 cm. The quartz was cut to satisfy index-matching requirements, and a search for the microwave radiation was performed with a sensitive bolometer. The null result of their experiment would indicate that the magnitude $X_{11}^0 < 10^{-9}$ esu, to be contrasted with the expected value of 2.7×10^{-9} esu given above.

Blackwell, Colegrove, and Walters[12] have performed a series of experiments in which a ruby-laser beam of one kilowatt intensity was amplitude modulated at 9 kMc with a Kominow modulator. The modulated beam was projected through various crystals situated in a microwave cavity to which was coupled a very sensitive superhetrodyne receiver tuned to 9 kMc. From their null results they estimate that the relevant coefficients in KDP are probably less than half the values listed above.[12a]

V.5. Surface Harmonics

A system which consists of two different media separated by a plane boundary does not have a center of inversion. This implies that a nonzero third-rank tensor may be associated with the system so that second-harmonic generation is allowed, whatever the point symmetries of the two constituent media. More physically, the magnitude of the displacement of an electron near the surface in the dielectric depends, not only on the magnitude of the optical electric field, but also on its direction. This picture also indicates that only a few molecular layers of the dielectric can contribute, so that the second-harmonic radiation will be modest compared with the bulk effects described previously.

Edwards *et al.*[13] have reported second-harmonic generation by an extensive list of surfaces. Terhune *et al.* (T62) during their experiments with calcite to be described in Sec. V.6 noticed that the second-harmonic radiation had a contribution which was in phase with the dc electric field induced bulk effect but whose magnitude was independent of that field. The slow variation in magnitude with the angle of incidence of the laser beam for the field-independent contribution contrasted with the sharp angular dependence of the bulk effect near the index-matching angle. The effect was virtually eliminated when the calcite crystal was immersed in a liquid of the same refractive index. These observations are consistent with the interpretation that surface production of second harmonic occurred.

The reader is referred to the paper of Bloembergen and Pershan (BP 62) for a detailed discussion of light waves at the boundaries of nonlinear media.

V.6. Higher-Order Effects

Evidence for several higher-order effects has come from an elegant series of experiments by Terhune *et al.* (T62). All third-rank tensor susceptibilities and their associated effects vanish, as the crystal has a center of symmetry but effects with fourth-rank tensor coefficients are not forbidden.

The third-harmonic production process is characterized by a fourth-rank tensor $\mathbf{X}^{3\omega}$ where

$$p_i^{3\omega} = X_{ijkl}^{3\omega}E_j^{\omega}E_k^{\omega}E_l^{\omega} .$$

About 10^4 third-harmonic photons were produced per laser pulse and the magnitude of the relevant elements of $X_{ijkl}^{3\omega}$ were estimated to be $\sim 10^{-15}$ esu.

Second-harmonic production induced by the presence of a dc electric field is characterized by a fourth-rank tensor $\mathbf{X}'^{2\omega}$ where

$$p_i^{2\omega} = X_{ijkl}'^{2\omega}E_j^0E_k^{\omega}E_l^{\omega} .$$

[10] These data are for the "unclamped" electro-optic effect. For comparison with experiments at difference frequencies large compared with mechanical resonances (say > 1 Mc) all the numbers in Eq. (V.4) should be reduced by about 10% [H. Jaffe (private communication)].

[11] J. Giordmaine (private communication).

[12] G. K. Walters (private communication).

[12a] *Note added in proof.* The dc effect has recently been observed by M. Bass, P. A. Franken, J. F. Ward, and G. Weinreich. (Phys. Rev. Letters 9, 446, 1962.) The beam from a 1 MW "giant-pulse" laser was projected through a sample of KDP which formed the dielectric of a parallel plate capacitor. The induced voltages were found to be in reasonable agreement with values predicted from the data of Sec. V.4. The dependence of the voltage on the plane of polarization of the laser beam, and the relative magnitude of the effect in KDP and deuterated KDP are in good agreement with theory.

[13] D. F. Edward, J. G. Mavroides and B. Lax, Bull. Am. Phys. Soc. 7, 14 (1962). These data were presented orally and are not surveyed in the abstract.

When a dc electric field of up to 250 kV/cm was applied to the crystal transverse to the incident ruby laser light beam, significant second-harmonic production was observed. The second-harmonic intensity was proportional to the square of the dc electric field, which is consistent with the above equation. The same qualitative features were observed for each of two incident beam directions—both satisfying the phase matching condition and the magnitudes of the relevant elements $\mathrm{X}''^{2\omega}_{ijkl}$ were estimated to be $\sim 10^{-15}$ esu.

As the dc electric field was reduced, another small contribution to the second-harmonic radiation in phase quadrature with the dc-induced radiation became apparent. This is consistent with the processes

$$p_i^{2\omega} = \mathrm{X}'^{2\omega}_{ijkl}\hat{k}_j E_k^{\omega} E_l^{\omega}$$

and

$$q_{ij}^{2\omega} = \eta_{ijkl}^{2\omega} E_k^{\omega} E_l^{\omega} .$$

between which the experiment was not able to distinguish. The magnitude of the relevant elements of $\mathrm{X}'^{2\omega}_{ijkl}$ or $\eta^{2\omega}_{ijkl}$ were estimated to be 10^{-18} esu.

V.7. Parametric Amplification

Nonlinear optical effects provide two approaches to the problem of using an optical source to provide coherent radiation at a lower frequency. One, which has been discussed in Sec. V.3, is the mixing of two sources to give a difference frequency. The other is to use the coherent source to provide pump power for the parametric amplification of lower frequencies in a nonlinear material. An important feature of parametric amplification is that it takes place for two frequencies simultaneously, ω_S and ω_I (referred to as "signal" and "idler" frequencies) which are related to the pump frequency ω_P by $\omega_P = \omega_S + \omega_I$. The technique is appealing because the frequency of the radiation generated (or rather, the frequency of the "noise" which is selectively amplified) is in principle continuously variable over a considerable range. The severe experimental problems lie in devising a geometry for the systems which, with the dispersion of the medium, permit the index matching condition to be satisfied. The conversion efficiency for an ideal configuration is ultimately limited by the Manley–Rowe relations. Kingston (Ki62) and Kroll (Kr62) have suggested ingenious arrangements which, to our knowledge, have not yet been experimentally realized.

For pedagogic purposes a schematic representation of the parametric process is now given which makes the following grossly simplifying assumptions [see (Ki62), (A62), and (Kr62) for more sophisticated discussions.]: (i) $\omega_I = \omega_S = \frac{1}{2}\omega_P = \frac{1}{2}\omega$ that is, the subharmonic is being amplified; (ii) The nonlinear material has a permeability and linear dielectric constant both equal to unity at all frequencies. This removes from the discussion the possibility of phase mismatching between pump and signal fields. It is not to be inferred from this assumption that the practical problems which arise because of dispersion are insignificant; (iii) The tensor character of the nonlinear susceptibility is ignored. Choosing phases so that a real positive amplification results, plane waves at pump and signal frequencies in the medium are taken as

$$\begin{aligned} \mathbf{E}_p &= \hat{x}\rho_p \sin\omega(t - z/c) , \\ \mathbf{E}_s &= \hat{x}\rho_s(z) \cos\tfrac{1}{2}\omega(t - z/c) \\ \mathbf{H}_s &= \hat{y}\rho_s(z) \cos\tfrac{1}{2}\omega(t - z/c) . \end{aligned} \qquad \text{(V.5)}$$

$\rho_s(z)$ is a slowly varying function of z representing the amplification and ρ_p is taken independent of z, as the interaction between pump and signal is small.

The nonlinear susceptibility X of the element mixes pump and signal fields to produce a contribution to the nonlinear polarization with x component p_x given by

$$\begin{aligned} p_x &= \mathrm{X}\rho_p\rho_s(z) \cos\tfrac{1}{2}\omega(t - z/c) \sin\omega(t - z/c) \\ &= \tfrac{1}{2}\mathrm{X}\rho_p\rho_s(z)\{\sin\tfrac{3}{2}\omega(t - z/c) + \sin\tfrac{1}{2}\omega(t - z/c)\} \end{aligned}$$

giving a polarization $\mathbf{P}_s$ at the signal frequency

$$\mathbf{P}_s = \tfrac{1}{2}\hat{x}\mathrm{X}\rho_p\rho_s(z) \sin\tfrac{1}{2}\omega(t - z/c) . \qquad \text{(V.6)}$$

This polarization does work on the signal wave and so amplifies it. The two waves are incident on a nonlinear element of unit cross section in the xy plane and we consider energy balance at the signal frequency for the volume bounded by planes $z = 0$, $z = \Delta z$. $\mathbf{S}_1$ and $\mathbf{S}_2$ are the outward normals at $z = 0$ and $z = \Delta z$, respectively.

$$\frac{c}{4\pi}\int_{\mathbf{S}_1+\mathbf{S}_2}(\mathbf{E}_s \times \mathbf{H}_s)\cdot d\mathbf{S} = \frac{1}{8\pi}\frac{\partial}{\partial t}\int_V (\mathbf{E}_s^2 + \mathbf{H}_s^2)dV + \int_V \mathbf{E}_s \cdot \frac{d\mathbf{P}_s}{dt}\, dV . \qquad \text{(V.7)}$$

The terms are, respectively, energy flow out of the element, energy stored in the element, and work done by the nonlinear polarization. Inserting Eqs. (V.5) and (V.6) into Eq. (V.7) and taking time averages over an integral number of cyles yields

$$\frac{1}{\rho_s(z)}\frac{\partial\rho_s(z)}{\partial z} = \frac{\pi\omega}{2c}\mathrm{X}\rho_p . \qquad \text{(V.8)}$$

Integration of Eq. (V.8) gives

$$\rho_s(z) = \rho_s(0)e^{z/L} \tag{V.9}$$

where $\rho_s(0)$ is the signal field amplitude at $z = 0$ and L is the characteristic length for amplification by a factor e:

$$L = (2c/\pi\omega)\cdot(1/\mathrm{X}\rho_p) \tag{V.10}$$

For a ruby laser delivering 5 J per cm² in 5×10^{-4} sec and estimating $\mathrm{X} = 10^{-10}$ esu we obtain

$$L \cong 2 \times 10^4 \text{ cm}. \tag{V.11}$$

The effect is therefore very small in the traveling wave case. Various embodiments employing resonant structures are considered by Kingston (Ki62) and Kroll (Kr62) and are shown to be nearer feasibility.

V.8. Two-Photon Excitation

Kaiser and Garrett (KG62) have observed the very interesting process of real two-photon absorption in CaF_2:Eu^{2+}. In these experiments ruby-laser light (6943 Å) was focused into a thin slab of CaF_2:Eu^{2+} located at the entrance slit of a spectrograph. The light transmitted by the crystal was found to contain blue ($\sim$ 4250 Å) light as well as the incident laser radiation. This effect was due to a process involving two (6943 Å) photon absorption to a real excited level, followed by nonradiative decay to an intermediate lower level and subsequent emission of 4250 Å radiation from that level to the ground state.

The absorption of the laser radiation ($\sim$ 14 000 cm^{-1}) is interpreted as a two-photon process because the lowest-lying levels in the crystal are at 22 000 cm^{-1} and, most importantly, the observed intensity of the blue light was found to vary quadratically with the intensity of the incident radiation. The observed magnitude of the effect is in satisfactory agreement with a theoretical discussion of the process (Kl62c).

This process differs significantly from the lowest-order second-harmonic production in that it involves four rather than three (real and virtual) levels, so that the restrictions imposed by symmetry considerations are entirely different. In particular, the relevant levels may now be eigenstates of parity so that the effect can be observed in crystals such as CaF:Eu^{2+} which have a center of inversion.[13a,13b]

[13a] *Note added in proof.* Two photon excitation has recently been observed in a vapor of atomic cesium by I. D. Abella. [Phys. Rev. Letters **9**, 453 (1962).] The $6S_{1/2}$–$9D_{3/2}$ transition ($\sim$3470 Å) was excited with a ruby laser ($\sim$6940 Å), and the subsequent emission of $9D_{3/2}$–$6P_{3/2}$ radiation at $\sim$5850 Å was detected. Thermal tuning of the laser frequency was exploited in order to achieve the two photon resonance condition. The numerical results of this experiment are in reasonable agreement with theory.

[13b] *Note added in proof.* The striking discovery of stimulated Raman scattering from organic liquids has recently been reported by G. Eckhardt, R. W. Hellwarth, F. J. McClung, S. E. Schwarz, D. Weiner, and E. J. Woodbury. [Phys. Rev. Letters **9**, 455 (1962).] The liquid was contained within the optical cavity of a $\sim$1 MW "giant-pulse" ruby laser. In this arrangement the intensity of the stimulated Raman emission is proportional to the product of the Raman and ruby radiation intensities in the liquid, and both radiated beams have the same spatial characteristics. Conversion efficiencies as high as 10% are reported.

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