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Study of Optical Third-Harmonic Generation in Reflection

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This paper reports studies of optical third-harmonic generation reflected from the boundary of solids including metals, semiconductors, alkali halides, and glass. The harmonic wave generated in reflection was found to interfere with those generated in air and in various optical components along the path of the incident laser beam. By studying the interference pattern, reliable relative values for the third-harmonic coefficients were deduced for alkali halides and compared with previous measurements of the coefficients for nonresonant three-wave mixing. It is found that the optical anisotropy is small for these cubic crystals. Preliminary results for metals and semiconductors indicate that the coefficients for these materials are of the correct order of magnitude expected of the nonlinearities associated with the conduction and bound electrons.

I. INTRODUCTION

ALTHOUGH optical third-harmonic generation (THG) has been observed in a variety of materials including solids,[1] liquids,[2,3] and gases,[4] quantitative study of this effect has been hampered by the breakdown of samples placed near the focus of the laser beam, and by the fact that harmonic waves generated at different parts of the focal region tend to cancel each other.[4] Chang and Galbraith[3] used an unfocused laser beam to demonstrate the enhancement of harmonic generation due to phase matching in liquids, but their detection sensitivity was insufficient to afford study of THG under general index-mismatched condition.[5]

This paper reports studies of THG reflected from the boundary of alkali halides, glass, metals, and semiconductors. In Sec. II, the nonlinear susceptibility coefficients for cubic crystals are introduced phenomenologically and discussed in the light of the quantum-mechanical expression derived for these coefficients. Section III describes the experimental setup and analyzes the interference effects between the harmonic waves generated at the boundary of the sample, in the air, and in other optical components along the path of the unfocused laser beam. The results deduced from the analysis are summarized and discussed in Sec. IV.

II. NONLINEAR SUSCEPTIBILITY COEFFICIENTS

In a cubic crystal with inversion symmetry the lowest-order nonlinear optical effects are those associated with an induced polarization, third-order in the electric field strength. This induced polarization contains a Fourier component at the third-harmonic frequency 3ω of the incident field $\mathbf{E}(\omega)$, whose ith Cartesian component is given phenomenologically as[1]

$$P_i(3\omega)=3\chi_{1122}^{(3)}(-3\omega,\omega,\omega,\omega)|\mathbf{E}(\omega)|^2E_i(\omega)+[\chi_{1111}^{(3)}(-3\omega,\omega,\omega,\omega)-3\chi_{1122}^{(3)}(-3\omega,\omega,\omega,\omega)]E_i^3(\omega). \quad (1)$$

Here $\chi_{1111}^{(3)}(-3\omega,\omega,\omega,\omega)$ and $\chi_{1122}^{(3)}(-3\omega,\omega,\omega,\omega)$ are the frequency-dependent nonlinear susceptibility coefficients. For an isotropic medium $\chi_{1111}^{(3)}(-3\omega,\omega,\omega,\omega)=3\chi_{1122}^{(3)}(-3\omega,\omega,\omega,\omega)$, so that there is only one independent nonvanishing coefficient. When the frequency ω of the incident field is sufficiently remote from the characteristic frequencies of the medium, these coefficients for THG should become identical to those for nonresonant three-wave mixing, namely, the coefficients responsible for the generation of the combination frequencies $\omega_1\pm\omega_2\pm\omega_3$, with no difference and sum frequencies of any two of the incident frequency components ω_1, ω_2, and ω_3 being near any of the characteristic frequencies of the medium. Furthermore, for media such as inert gases at low pressure, where the nonlinear optical effects arise primarily from the distortion of the electronic distribution of the spherical gas molecules,[4] the third-harmonic coefficients should also be identical to those describing the optical Kerr effect and effects associated with the intensity-dependent changes in the refractive index.[6]

Much insight may be gained into the nature of the third-harmonic coefficients by considering the response of a molecule to an incident field in the electric dipole approximation. Using the method of Bogoliubov generalized to include time-dependent perturbation,[7] one derives the following expression for $\chi_{1111}^{(3)}(-3\omega,\omega,\omega,\omega)$:

$$\chi_{1111}^{(3)}(-3\omega,\omega,\omega,\omega)=\frac{e^4}{\hbar^3}\Big(\sum_{\substack{k,n\\ l\neq0}}\langle0|x|k\rangle\langle k|x|l\rangle\langle l|x|n\rangle\langle n|x|0\rangle D_{kln}-\sum_{k,n}\langle0|x|k\rangle\langle k|x|0\rangle\langle0|x|n\rangle\langle n|x|0\rangle D_{k0n}\Big), \quad (2)$$

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[1] P. D. Maker, R. W. Terhune, and C. M. Savage, in *Proceedings of the Third International Conference on Quantum Electronics, Paris, 1963*, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964), p. 1559; P. D. Maker and R. W. Terhune, Phys. Rev. **137**, A801 (1965).

[2] P. P. Bey, J. F. Giuliani, and H. Rabin, Phys. Rev. Letters **19**, 819 (1967).

[3] R. K. Chang and L. K. Galbraith, Phys. Rev. **181**, 993 (1968).

[4] G. H. C. New and J. F. Ward, Phys. Rev. Letters **19**, 556 (1967).

[5] Contrary to the difficulties encountered in the optical region, THG in the infrared has been successfully studied using a CO_2 laser. N. VanTran, J. H. McFee, and C. K. N. Patel, Phys. Rev. Letters **21**, 735 (1968).

[6] C. C. Wang, Phys. Rev. **152**, 149 (1966).

[7] K. M. Case, Progr. Theoret. Phys. (Kyoto) Suppl. **37**, 1 (1966).

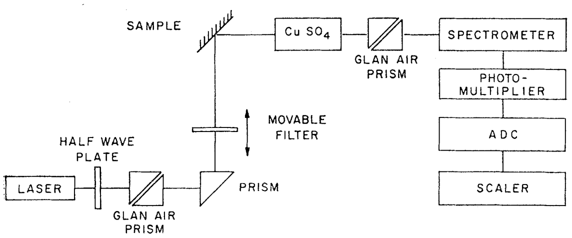

FIG. 1. Schematic of the experimental setup.

$$D_{kln}=\frac{1}{4}\left[\frac{1}{(\omega_{n0}+\omega)(\omega_{l0}+2\omega)(\omega_{k0}+3\omega)}+\frac{1}{(\omega_{n0}-\omega)(\omega_{l0}-2\omega)(\omega_{k0}-3\omega)}+\frac{1}{(\omega_{n0}-\omega)(\omega_{l0}+2\omega)(\omega_{k0}+\omega)}+\frac{1}{(\omega_{n0}+\omega)(\omega_{l0}-2\omega)(\omega_{k0}-\omega)}\right], \quad (3)$$

$$D_{k0n}=\tfrac{1}{4}(\omega_{k0}+3\omega_{n0})/(\omega^2{}_{n0}-\omega^2)(\omega^2{}_{k0}-9\omega^2), \quad (4)$$

with similar expression for $\chi_{1122}{}^{(3)}(-3\omega, \omega, \omega, \omega)$ and other third-order susceptibility coefficients. Here, $\hbar\omega_{k0}=\hbar(\omega_k-\omega_0)$ is the energy difference between the kth excited state and the ground state, etc. It is instructive to examine the limiting form of Eq. (2) for certain simple physical systems. For example, Eq. (2) is identically zero for a system of harmonic oscillators, as may be verified by substituting in it the known matrix elements between the energy states of an harmonic oscillator. For a one-dimensional anharmonic oscillator with a Hamiltonian of the form

$$H=(1/2m)(p^2+m\omega_0{}^2x^2)+\eta\hbar\omega_0(x/x_0)^4, \quad (5)$$

where ω_0 and $x_0=(\hbar/m\omega_0)^{1/2}$ are, respectively, the angular frequency and radius of the corresponding classical harmonic oscillator, an approximate expression for $\chi_{1111}{}^{(3)}(-3\omega, \omega, \omega, \omega)$ may be obtained by substituting in Eq. (2) a set of approximate wave functions for the anharmonic oscillator.[8] To first order in the anharmonicity coefficient η, one derives

$$\chi_{1111}{}^{(3)}(-3\omega, \omega, \omega, \omega)=-\eta\frac{e^4}{\hbar^3}\frac{x_0{}^4\omega_0{}^5}{(\omega_0{}^2-\omega^2)^3(\omega_0{}^2-9\omega^2)}. \quad (6)$$

Equation (6) is identical to the classical expression derived by Armstrong *et al.*[9] One observes from Eq. (6) that the third-harmonic coefficient may either be positive or negative, depending on the sign of the anharmonicity coefficient. For a two-level system with electric dipole allowed transition, the first summation in Eq. (2) is always zero, and so the third-harmonic coefficient is negative. However, the potential function of a free atom is usually such that the anharmonicity coefficient η is negative, leading to a positive value for the third-harmonic coefficient.

III. ANALYSIS OF THE OBSERVED HARMONIC WAVES

The experiments were performed with the unfocused laser beam near 1.06 μ from a Nd^{3+}-doped glass laser Q-switched by a rotating prism and fired at a repetition rate of one pulse every 4 sec. The output from the laser was approximately 0.18 J in energy, 0.05 cm^2 in cross section, and 70 nsec in duration. The experimental arrangement is depicted schematically in Fig. 1. The output from the laser was incident upon the sample, with its state of polarization determined by the orientation of the half-wave plate and the Glan-air prism. The third-harmonic wave reflected from the sample surface was analyzed with another Glan-air prism, filtered through a cell of CuSO$_4$ solution and a spectrometer, and detected with a high-gain photomultiplier combined with an analog-to-digital converter (ADC) and scaler circuits. Freshly cleaved (100) surfaces were used for all alkali-halide samples, and results were reproducible to within about 15% for all but KI samples. For samples of KI crystals, prevention of sample breakdown necessitated experimentation with a highly attenuated laser beam; the corresponding yield varied over a wide range, making it difficult to deduce the third-harmonic coefficient (see below).

It was found early in the experiments that a substantial amount of third-harmonic power was generated in the air and in various optical components along the path of the unfocused laser beam. A combination of glass filters (Corning glass filters No. 7-57 and No. 3-72) were thus placed in front of the sample surface to eliminate the third-harmonic wave generated along that portion of the beam path before the glass filters. At the various angles of incidence ($\theta_i=30°$, 45°, and 60°) used in the experiments, the laser intensity reflected from the samples was sufficiently low so that the third-harmonic wave generated along the beam path after the sample surface could be neglected. This implied that the detected third-harmonic power resulted from the addition in amplitudes of the third-harmonic waves generated at the sample, in the air between the sample and the glass filters, and near the exit face of the glass filters. With the laser beam polarized perpendicular to the plane of incidence, the component of the third-harmonic wave polarized perpendicular to the plane of reflection $E_\perp(3\omega)$ is given by

$$E_\perp(3\omega)=-4\pi E_0{}^3(\omega)F^3f(\theta_i)\{[(A-B)+B\cos4\alpha]-h\chi_f{}^{(3)}e^{-i\Delta kl}-ih(k/\Delta k)\chi_a{}^{(3)}\times e^{-i\Delta kl/2}\sin(\Delta kl/2)\}, \quad (7)$$

$$F=2\cos\theta_i/(n_1\cos\theta_1+\cos\theta_i), \quad (8)$$

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[8] E. Hutchisson, Phys. Rev. **37**, 45 (1931).

[9] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 171 (1962).

$$f(\theta_i)=1/(n_1\cos\theta_1+n_3\cos\theta_3)(n_3\cos\theta_3+n_3\cos\theta_3)\,, \quad (9)$$

$$r=(n_3\cos\theta_3-\cos\theta_i)/(n_3\cos\theta_3+\cos\theta_i)\,, \quad (10)$$

$$h=r/[F^3f(\theta_i)]\,, \quad (11)$$

with $n_1\sin\theta_1=n_3\sin\theta_3=\sin\theta_i$, and n_3 and n_1 being the refractive indices of the sample at the fundamental and third-harmonic frequencies, respectively. Here, F and $f(\theta_i)$ are, respectively, the linear and nonlinear Fresnel factors[10];

$$A=\chi_{1111}^{(3)}(-3\omega,\omega,\omega,\omega)$$

and

$$B=\tfrac{1}{4}[\chi_{1111}^{(3)}(-3\omega,\omega,\omega,\omega)-3\chi_{1122}^{(3)}(-3\omega,\omega,\omega,\omega)]$$

for the sample; α is the angle between $\mathbf{E}(\omega)$ and the [010] axis in the plane of the sample surface; $E_0(\omega)$ is the amplitude of the incident field; $\chi_a^{(3)}$ is the third-harmonic coefficient of air; $\chi_f^{(3)}$ and θ_f describe, respectively, the amplitude and phase of the third-harmonic wave generated near the exit face of the glass filters; $k=3\omega n_3/c$ and $\Delta k=3\omega(n_3-n_1)/c$ for air; and l is the length of the beam path between the glass filters and the sample surface. By changing the length l, the third-harmonic power reflected from the sample surface was found to oscillate sinusoidally with a period equal to twice the coherence length, $l_{\mathrm{coh}}=\pi/\Delta k$, calculated with the known refractive indices of air[11] (Fig. 2). It can be shown by straightforward manipulation that such a behavior is predicted by Eq. (7).

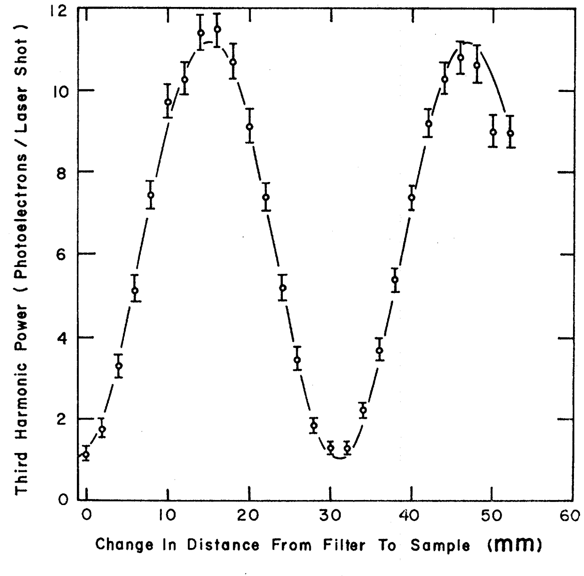

FIG. 2. Oscillatory behavior of the reflected third-harmonic power observed by changing the distance between the glass filters and the sample surface. The period observed is equal to twice the coherence length $l_{\mathrm{coh}}=\pi/\Delta k$ calculated with the known refractive indices of air.

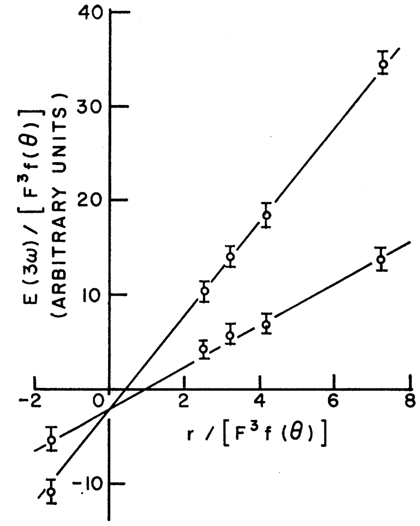

FIG. 3. Plot of Eqs. (12) and (13) with the values of $E_{\max}$ and $E_{\min}$ deduced from the measured values of harmonic power at $\theta_i=30°$, 45°, and 60°. The two pairs of points with the lowest h values were obtained with $\mathbf{E}(\omega)$ polarized in the plane of incidence and with F and $f(\theta_i)$ replaced by the corresponding linear and nonlinear Fresnel factors. (See Ref. 10.) The error bar indicates the experimental uncertainty.

To determine the coefficient $A=\chi_{1111}^{(3)}(-3\omega,\omega,\omega,\omega)$, the sample was oriented with $\alpha=0$. The distance l was then changed to determine the maximum and minimum of the third-harmonic power reflected from the sample surface at the various angles of incidence. In terms of the electric field strength $E_{\max}$ and $E_{\min}$ corresponding to the observed extrema of the reflected harmonic power, one obtains from Eq. (7)

$$[(k/2\Delta k)\chi_a^{(3)}+\chi_f']h-A = \pm E_{\max}/[4\pi E_0^3(\omega)F^3f(\theta_i)] \quad (12)$$

and

$$[(k/2\Delta k)\chi_a^{(3)}-\chi_f']h-A = \pm E_{\min}/[4\pi E_0^3(\omega)F^3f(\theta_i)]\,, \quad (13)$$

where

$$\chi_f'=[(k/2\Delta k)^2\chi_a^{(3)2}+\chi_f^{(3)2}-(k/\Delta k)\chi_a^{(3)}\chi_f^{(3)}\cos\theta_f]^{1/2}.$$

Thus, according to Eqs. (12) and (13), the plot of $E_{\max}/[F^3f(\theta_i)]$ and $E_{\min}/[F^3f(\theta_i)]$ as functions of h should yield straight lines (Fig. 3). Whereas the common intercept on the vertical axis gives the value of A for the sample, the sum of the slope of these two straight lines gives the value of $(k/\Delta k)\chi_a^{(3)}$ for air, from which the value of $\chi_a^{(3)}$ can in turn be determined.

Attempts to measure the coefficient B were made by changing the angle α between $E(\omega)$ and the crystallographic axis, with $\theta_i=30°$ and the distance l set to give maximum reflected harmonics. According to Eq. (7) with $A\gg B$, this should produce amplitude modulation of the form of $\cos 4\alpha$ in the observed harmonic power. Alternatively, one could deduce B by studying the

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[10] N. Bloembergen and P. S. Pershan, Phys. Rev. **128**, 606 (1962).

[11] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Co., Cleveland, Ohio, 1960), 42nd ed., p. 2943.

TABLE I. Values of the third-harmonic coefficients.

Material	$\chi_{1111}^{(3)}(-3\omega, \omega, \omega, \omega)$ (10^{-14} cm^3/erg)	$\chi^{(3)}(-(\omega+\Delta), \omega, \omega, -(\omega-\Delta))$ (10^{-14} cm^3/erg)
LiF	0.6	0.2[a]
NaF	0.5	
BSC glass	0.8	1.3[a]
NaCl	0.6	1.7[a]
KCl	1.2	1.9[a]
KBr	1.4	3.0[a]
MgO	2.4	1.0[a]
air	4.1×10^{-5}	13×10^{-5}[b]

[a] Reference 1.
[b] Reference 12; values for N_2 and O_2 at 1 atm gas pressure are taken for comparison.

dependence on α of the component of $\mathbf{E}(3\omega)$ polarized in the plane of reflection. But no signal discernible from the experimental uncertainty could be found in either case.

IV. RESULTS AND DISCUSSIONS

Figure 3 shows the plot of Eq. (12) and (13), with the values of $E_{\max}$ and $E_{\min}$ deduced from the harmonic powers measured for Borosilicate glass at $\theta_i=30°$, $45°$, and $60°$. The signs in these equations were chosen so that the coefficient $\chi_a^{(3)}$ for air was positive. Similar plots were obtained for a number of alkali-halide crystals. As expected, the values of $\chi_a^{(3)}$ deduced from these various plots were the same to within the experimental accuracy. The coefficients $\chi_{1111}^{(3)}(-3\omega, \omega, \omega, \omega)$ deduced for these crystals were found to have the same sign as the coefficient $\chi_a^{(3)}$ for air, with a relative uncertainty of about $\pm30\%$. In view of the lack of precise knowledge on the temporal and spatial behavior of the laser, the absolute values of these coefficients are estimated to be accurate to within a factor of 3. The numerical values for the coefficient are summarized in Table I.

It is interesting to compare these results in Table I with the corresponding values of $\chi^{(3)}[-(\omega+\Delta), \omega, \omega, -(\omega-\Delta)]$ obtained in Ref. 1 and Ref. 12 with a Q-switched ruby laser. These values are reproduced here in Column 3 of Table I. As discussed earlier, these two sets of results should be the same in the absence of dispersion. One observes in Table I that within the experimental accuracy of the measurements the relative magnitudes for these two sets of measurements are in reasonable agreement for all materials but LiF and MgO. Rough estimates show that the difference of about a factor of 2 in the coefficients for the latter two materials may be accounted for by the dispersive effects associated with the electronic and lattice resonances in these materials.

Attempts were also made to study THG reflected from metal and semiconductor surfaces. Here the analysis was complicated as the coefficient for these materials became complex and the sample reflectivity was high so that the harmonic waves generated along the beam path after the sample surface could no longer be neglected. Preliminary results with Ag, Au, Si, and Ge indicate that the coefficients are of the order of 10^{-12} cm^3/erg or less, comparable in magnitude to what is expected for the nonlinearities of the conduction and bound electrons.[13]

Based on the lack of discernible amplitude modulation in the observed third-harmonic power, an upper limit was placed for the B coefficient of the various materials investigated. This upper limit is 10^{-15} cm^3/erg for MgO and 10^{-16} cm^3/erg for LiF and other materials.

In conclusion, the coefficient $\chi_{1111}^{(3)}(-3\omega, \omega, \omega, \omega)$ for THG has been deduced for a number of cubic crystals and for air. This set of coefficients is in reasonable agreement with that deduced previously from nonresonant three-wave mixing experiments. The technique employed in this work can be extended to study THG from gases by arranging to vary the gas and its pressure between the glass filters and the sample surface.

The authors are indebted to R. W. Terhune for many helpful discussions and critical comments on the manuscripts, and to G. W. Ford for discussions on the Bogoliubov perturbation theory.

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[12] W. G. Rado, Appl. Phys. Letters **11**, 123 (1967).

[13] P. A. Wolff and G. A. Pearson, Phys. Rev. Letters **17**, 1015 (1966); P. A. Wolff, Phys. Rev. **171**, 436 (1968); S. S. Jha and N. Bloembergen, *ibid.* **171**, 891 (1968).