Contributions to Optical Nonlinearity in GaAs as Determined from Raman Scattering Efficiencies

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Values for the electro-optic and second-harmonic-generation coefficients [r_{41} and d_{14}(SHG)] can be calculated from absolute spontaneous-Raman-scattering data alone. The ratio of electronic and lattice contributions to r_{41}, and the stimulated Raman gain coefficients for the LO and TO modes, may also be obtained. The technique is applied to GaAs and the value for r_{41} [$(1.5\pm0.1)\times10^{-12}$ m/V] agrees with direct measurements, while the value for d_{14}(SHG) [$(1.4\pm0.1)\times10^{-10}$ m/V] is within the range of some direct SHG measurements.

THE nonlinear optical properties of insulating crystals are derived from two sources: first, the perturbation of the optical polarizability by an electromagnetic field acting through a lattice displacement (lattice or deformation potential interaction); second, the perturbation of the optical polarizability produced by the direct action of the field on the electronic energy levels (nonlattice or electronic interaction).

In piezoelectric crystals with only one simultaneously Raman- and infrared-active mode of given symmetry type, measurement of the absolute scattering efficiencies for longitudinal and transverse modes S_L and S_T and the corresponding frequencies is sufficient to determine separately the lattice and electronic contributions, their ratio C, the electro-optic coefficient r_{ijk}, the nonlinear coefficient d_{kji}(SHG), and, with the measured linewidths 2Γ, the gain coefficients for stimulated Raman phonon or polariton scattering. The technique is applied to high-purity GaAs and the result is found to agree with previous measurements of r_{123} and C but contradicts an earlier second-harmonic-generation measurement of d_{123}(SHG). Several other techniques have been employed in the past to determine the absolute contributions of the lattice and nonlattice terms to electro-optic nonlinearity in $LiNbO_3$ [1] and GaAs [2] and the relative contributions in GaP [3] and ZnSe.[4]

In the case of semiconductors (where the macroscopic field may be regarded also as the "local" field), Loudon[5] has shown that both lattice and electronic interactions contribute to the Raman scattering efficiency for longitudinal modes (S_L) but that only the lattice interaction contributes to the scattering efficiency for transverse modes (S_T). It should be noted that what Loudon terms an electro-optic coefficient (z_{ijk}) is, in fact, only the electronic (nonlattice) contribution ($\xi_{ijk}/\epsilon_0 n^4$ in the notation of Refs. 1, 7, and 8) to the conventional electro-optic coefficient (r_{ijk}).[1] In ionic crystals where the Lorentz field is the appropriate local field,[6] the technique also applies, although some care must be taken to identify coefficients based on macroscopic parameters with microscopic interactions in a consistent fashion. When the crystal structure permits several simultaneously Raman- and infrared-active modes of the same symmetry (as in $LiNbO_3$), the present technique is complicated but determination of nonlinear coefficients from Raman data is possible in principle.[7]

We ignore plasmon and polariton effects (i.e., the plasma frequency is assumed much less than the TO frequency and the phonon wave vector is assumed much greater than the TO frequency divided by the velocity of light); then for crystals with zinc-blende structure the Raman efficiencies inside the medium are given by[1,5]

$$S_{L,T}=\sigma_{L,T}\rho^{-1}|d\alpha_{12}/dQ_3|^2_{L,T}, \tag{1}$$

with

$$\sigma_{L,T}=\frac{\hbar\omega_s^4(\bar{n}_{L,T}+1)ld\Omega}{32\pi^2\epsilon_0^2c^4\omega_{L,T}}, \tag{2}$$

where ρ is the reduced mass density, ω_T and ω_L the transverse and longitudinal mode frequencies, ω_s the Stokes frequency, $\bar{n}$ the Bose factor, l the scattering length, and $d\Omega$ the scattering solid angle.

The differential polarizability $d\alpha_{12}/dQ_3$ for the TO mode is $\partial\alpha_{12}/\partial Q_3\equiv\alpha_{123}$, and (introducing the notations of Refs. 1 and 2) for the LO mode, we have

$$\frac{d\alpha_{12}}{dQ_3}=\frac{\partial\alpha_{12}}{\partial Q_3}+\frac{\partial\alpha_{12}}{\partial E_3}\frac{\partial E_3}{\partial Q_3}$$

$$\equiv\alpha_{123}+\xi_{123}\beta_3^{-1}(\omega_L)\equiv\alpha_{123}[1-(aC)^{-1}], \tag{3}$$

[1] I. P. Kaminow and W. D. Johnston, Jr., Phys. Rev. **160**, 519 (1967); **178**, 1528(E) (1969).
[2] A. Mooradian and A. L. McWhorter, in *Proceedings of the International Conference on Light Scattering Spectra in Solids, New York University, 1968*, edited by G. B. Wright (Springer-Verlag, New York, 1969).
[3] W. L. Faust and C. H. Henry, Phys. Rev. Letters **17**, 1265 (1966).
[4] S. Ushioda, A. Pinczuk, W. Taylor, and E. Burstein, in *II-VI Semiconducting Compounds*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967); R. C. C. Leite, T. C. Damen, and J. F. Scott, in *Proceedings of the International Conference on Light Scattering Spectra in Solids, New York University, 1968*, edited by G. B. Wright (Springer-Verlag, New York, 1969) (note the definition of C in these papers is the inverse of that used here).
[5] R. Loudon, Advan. Phys. **13**, 423 (1964); in *Proceedings of the International Conference on Light Scattering Spectra in Solids, New York University, 1968*, edited by G. B. Wright (Springer-Verlag, New York, 1969).
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[7] W. D. Johnston, Jr. (to be published).

TABLE I. Comparison of electro-optic, optical rectification, and SHG coefficients from analysis of Raman scattering with those obtained from direct measurement.

r_{41} (10^{-12} m/V)	d_{14}(SHG) (10^{-10} m/V)	d_{14}(OR) (10^{-10} m/V)	C
1.5±0.1	1.4±0.1	0.55±0.03	−0.59[a]
1.5±0.3	1.0±0.2	0.55±0.1	−0.46[b]
1.5±0.2[c]	...	...	...
...	1.9±0.9[d]	...	...
...	3.7±1.3[e]	...	...
...	...	1.04±0.17[f]	...
...	...	0.69±0.13[f]	...

[a] This paper. [b] See Ref. 2. [c] See Ref. 15. [d] See Ref. 16. [e] See Ref. 17. [f] See Ref. 18.

where, neglecting damping,

$$\beta_3(\omega)=\left[\frac{\epsilon_0 n_\infty^2}{a\rho\omega_T^2}\right]^{1/2}\frac{\omega_T^2}{\omega_T^2-\omega^2}, \tag{4}$$

$$a=\omega_T^2(\omega_L^2-\omega_T^2)^{-1}, \tag{5}$$

n_∞ is the high-frequency refractive index, and C is the ratio of lattice and electron contributions at $\omega=0$, i.e., $C=\alpha_{123}\beta_3(0)/\xi_{123}$. The electro-optic coefficient at modulating frequency $\omega\rightarrow 0$ is given by[8]

$$\begin{aligned}-\epsilon_0 n^4 r_{123}&=\alpha_{123}\beta_3(0)+\xi_{123}\\&\equiv\alpha_{123}\beta_3(0)[1+C^{-1}],\end{aligned} \tag{6}$$

with n the refractive index at the optical frequency, which may differ from n_∞ in Eq. (4).

Combining these equations to find the nonlinear coefficients in terms of measured quantities yields

$$C^{-1}=a[1\pm(\sigma_T S_L/\sigma_L S_T)^{1/2}], \tag{7}$$

$$r_{ijk}^2=S_T n_\infty^2(1+C^{-1})^2/\epsilon_0 n^8 a\omega_T^2\sigma_T, \tag{8}$$

$$\xi_{ijk}=-\epsilon_0 n^4 r_{ijk}/(1+C). \tag{9}$$

The electronic nonlinear coefficient is related to quantities defined elsewhere[9] by $\xi_{ijk}=4\epsilon_0 d_{kji}(\mathrm{SHG})$ and $d_{123}\equiv d_{14}$, $r_{123}\equiv r_{63}=r_{41}$. The square root in (7) leads to a sign ambiguity that can be clarified as noted below. The scattering efficiencies and linewidths can be used to obtain phonon Raman gain coefficients[1,10] and, with C, polariton gain coefficients.[5,11]

A GaAs sample with edges along [100] axes having 3×10^{14} carriers/cm^3, a mobility of 5900 cm^2/V sec, and resistivity of 4 Ω cm was used in the experiments with 90° scattering geometry. After taking the geometry into account,[12] the efficiencies corresponding to α_{123} are

$$S_L/Ld\Omega=(2.3\pm0.2)\times10^{-6}\ \mathrm{cm^{-1}\ sr^{-1}},$$
$$S_T/Ld\Omega=(1.5\pm0.2)\times10^{-6}\ \mathrm{cm^{-1}\ sr^{-1}},$$
$$\omega_L=292\ \mathrm{cm^{-1}},\quad \omega_T=269\ \mathrm{cm^{-1}},$$
$$2\Gamma_L=1.6\ \mathrm{cm^{-1}},\quad 2\Gamma_T=1.7\ \mathrm{cm^{-1}}$$

for 1.06-μ excitation using measurement techniques described previously.[13] Because the plasma frequency is much less than ω_T, plasmons play no role.[2] From Eqs. (7)–(9), taking $n^2=12.1$ at 1.06 μ and $n_\infty^2=11.1$,[14] we calculate $r_{41}=(1.5\pm0.1)\times10^{-12}$ m/V, $C\equiv-0.59$, and $d_{14}(\mathrm{SHG})=(1.4\pm0.1)\times10^{-10}$ m/V. [In esu, $r_{41}=4.5\times10^{-8}$ and $d_{14}(\mathrm{SHG})=3.3\times10^{-7}$.]

The other solution is $r_{41}=30.75\times10^{-12}$ m/V, $C=+0.07$, and $d_{14}(\mathrm{SHG})=10.6\times10^{-10}$ m/V. A crude measurement of r_{41} or d_{14} serves to eliminate this solution. Alternatively, a qualitative inspection of Raman spectra for material with sufficient carrier density to permit observation of the plasmon–LO-phonon coupling[2] or of polariton spectra[4] would also suffice to eliminate this solution, which corresponds to constructive interference between the deformation potential and electronic nonlinearity terms.

The clamped electro-optic coefficient of semi-insulating GaAs has been measured directly by Turner[15] [$r_{41}=(1.5\pm0.15)\times10^{-12}$ m/V at 3.39 μ and 63 MHz] and is in good agreement with our first solution but not with the alternative solution. Our results for r_{41}, d_{14}(SHG), and C are in reasonable agreement with those of Mooradian and McWhorter obtained by a different technique.[2] Our value for d_{14}(SHG) agrees within experimental error with the (SHG) measurements of Wynne and Bloembergen[16] but disagrees with the value obtained by Patel.[17] The various values are compared in Table I, along with values for the optical rectification coefficient $d_{14}(\mathrm{OR})=\frac{1}{4}n^4 r_{41}$.[18] The nonlinear coefficients are expected to be only weakly wavelength-dependent for wavelengths greater than 1 μ, which is well removed from the band edge.[4,15]

The Raman phonon gain for a fundamental-mode 1.06-μ pump with confocal focusing in the crystal is calculated[10] to be 1.5%/W for a single pass. Although this gain is quite large by comparison with that of other solids,[19] our measurements on several GaAs

[8] I. P. Kaminow, in *Ferroelectricity*, edited by E. F. Weller (Elsevier Publishing Co., Amsterdam, 1967).
[9] G. D. Boyd and D. A. Kleinman, J. Appl. Phys. **39**, 359 (1968).
[10] G. D. Boyd, W. D. Johnston, Jr., and I. P. Kaminow, IEEE J. Quantum Electron. **QE5**, 203 (1969).
[11] C. H. Henry and C. G. B. Garrett, Phys. Rev. **171**, 1058 (1968).
[12] For $x(yz)y$ geometry, the observed LO and TO intensities must be multiplied by 2 to obtain (10), while for $x(yx)y$ the observed TO intensity may be used directly.
[13] W. D. Johnston, Jr., and I. P. Kaminow, Phys. Rev. **168**, 1045 (1968); **178**, 1528(E) (1969).
[14] B. O. Seraphin and H. E. Bennett (also M. Hass) in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic Press Inc., New York, 1967), Vol. 3.
[15] E. H. Turner (unpublished results); see also T. E. Walsh, RCA Rev. **27**, 323 (1966); E. H. Turner and I. P. Kaminow, J. Opt. Soc. Am. **5**, 3523 (1968).
[16] J. J. Wynne and N. Bloembergen, Phys. Rev., this issue, **188**, 1211 (1969).
[17] C. K. N. Patel, Phys. Rev. Letters **16**, 613 (1966).
[18] T. Y. Chang, N. VanTran, and C. K. N. Patel, Appl. Phys. Letters **13**, 357 (1968). The two values for d_{14}(OR) correspond to optical mixing measurements at difference frequencies of 53.5 and 54.3 GHz.
[19] W. D. Johnston, Jr., I. P. Kaminow, and J. G. Bergman, Jr., Appl. Phys. Letters **13**, 190 (1968).

samples at 1.06 μ indicate that the lowest absorption coefficient for currently available bulk material is ~ 0.7 cm^{-1}, which makes these crystals unsuitable for Raman oscillator applications with the Nd-YAG laser.

The method described here is well suited to measurements of r_{ijk} on wurtzite or zinc-blende-type crystals with conductivity too large to sustain low-frequency modulating fields. It also provides more accurate measurements of ξ_{ijk} than present high-power-pulsed SHG measurements.

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Measurement of the Lowest-Order Nonlinear Susceptibility in III–V Semiconductors by Second-Harmonic Generation with a CO_2 Laser*

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Both the magnitude and sign of the nonlinear susceptibility $d_{14}^{NL}(-2\omega,\omega,\omega)$ describing second-harmonic generation at 10.6 μ have been measured in wedge-shaped semiconducting samples using a Q-switched CO_2 laser. The results are (in units of 10^{-6} esu): $d_{14}=+1.0$ for InAs, $+0.45$ for GaAs, $+0.26$ for GaP, and $+1.5$ for GaSb. The limits of error are discussed, and the results are compared with previous experimental data and with several recent theoretical calculations. The effect of uniaxial compression on the coherence length for second-harmonic generation is also measured.

I. INTRODUCTION

THE nonlinear susceptibility describing second-harmonic generation in III-V and II-VI semiconductors was first measured in the visible and near-infrared region of the spectrum. Patel[1,2] first observed the second-harmonic generation (SHG) in these materials with a CO_2 laser beam. He pointed out the difficulties in obtaining accurate values for the nonlinearity which are associated with the long coherence length. He measured the transmission through a plane-parallel slab which could be rotated. This technique, first introduced by Maker *et al.*,[3] presents difficulties in high-index materials with long coherence lengths. It is difficult to control the geometry, and because of the high Fresnel reflection coefficient, significant changes in the fundamental intensity distribution are caused by the standing-wave pattern inside the plane-parallel slab. In addition, the absorption in samples which are many coherence lengths thick may be significant. The experimental corrections are large and uncertain. It should be pointed out that the observation of second harmonic (SH) in reflection obtained in the visible region is free from these uncertainties.[4] It is of considerable interest to obtain reliable values of the nonlinear susceptibility in the far infrared, because these values may be compared more readily with theoretical calculations. These make use of the low-frequency approximation, in which all energy denominators are replaced by an effective energy-band gap. Several of such calculations have recently been published for the simple structures of III-V and II-VI semiconductors. The experiments to be described in this paper were, in fact, a stimulus for these calculations. The results of the next-higher-order nonlinearity, describing third-order optical mixing, have already been published.[5]

The experimental method of determining both the magnitude and the sign of the susceptibility for SHG in these high-index materials is described in Sec. II. The determination of the sign is new and the results for the magnitude, believed to be more accurate, are compared with previous experimental results and with theoretical calculations in Sec. III. In a final section the effect of uniaxial compression on the coherence length is investigated. It was originally hoped that phase matching in these materials could be achieved in this manner, but the required uniaxial stresses are too large.

II. EXPERIMENTAL METHOD

The experimental difficulties associated with SHG in transmission through a plane-parallel plate of high-index material with small dispersion, mentioned in the Introduction, are discussed in more detail in Appendix A2 of the Ph.D. thesis of one of the authors (J.J.W.).[6]

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