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Interference of Resonant and Nonresonant Three-Wave Mixing in Diamond*

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We have used the second harmonic of a Nd:glass laser and a continuously tunable dye laser to measure the variation of the third-order nonlinear susceptibility $|\chi^{(3)}(-2\omega_1+\omega_2, \omega_1, \omega_1, -\omega_2)|^2$ when $\omega_1-\omega_2$ passes through the optical-phonon resonance in diamond. The frequency difference between the observed maximum and minimum determines the nonlinear electronic susceptibility $\chi^{(3)E}$ both in sign and magnitude with respect to the Raman susceptibility. A theoretical discussion of this interference is presented.

In centrosymmetric nonpolar crystals, the third-order nonlinear susceptibility $\chi^{(3)}(-\omega_3, \omega_1, \omega_1, -\omega_2)$ along with the wave-vector mismatch $\Delta k = 2k_1 - k_2 - k_3$ completely determines the light intensity at the combination frequency $\omega_3 = 2\omega_1 - \omega_2$.[1-3] When the frequencies ω_1, ω_2, ω_3 lie in the transparent region of the material but the intermediate difference frequency $\omega_1-\omega_2$ approaches that of the resonance of Raman-active optical phonons, the nonlinear susceptibility is the sum of a real nonresonant part due to purely electronic nonlinearities and a complex Raman susceptibility.[4] As the difference frequency is varied, the intensity at ω_3 goes through both a maximum and a minimum for each nondegenerate phonon mode. We have observed this behavior near the optical-phonon frequency in diamond. In our experiment the difference frequency $\omega_1-\omega_2$ was varied by tuning the output of a dye laser at ω_2. The field at the fixed frequency ω_1 was the second harmonic of a Nd:glass laser. The observed frequency difference between the maximum and minimum of the intensity at ω_3 permits an absolute determination of the sign and magnitude of the electronic contribution to the nonlinear susceptibility.

A diagram of the experimental apparatus is displayed in Fig. 1. The second harmonic of a Q-switched Nd:glass laser equipped with a three-

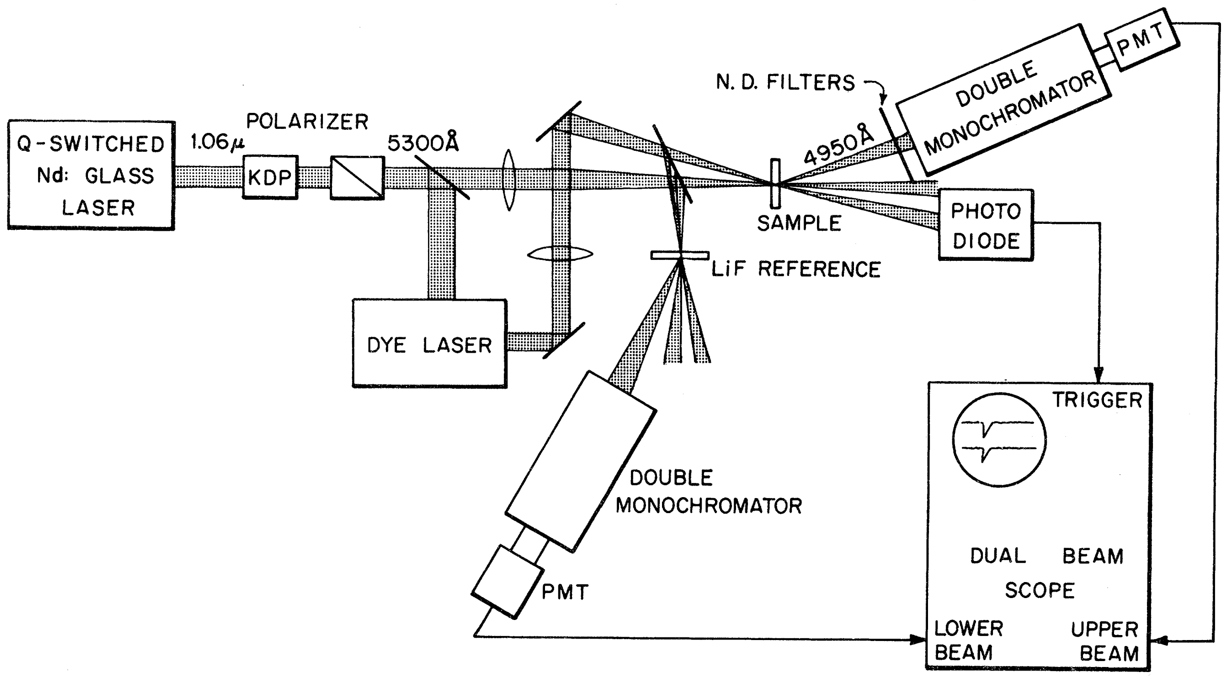

FIG. 1. Experimental apparatus for resonant three-wave mixing. A KDP (potassium dihydrogen phosphate) crystal is used to double the frequency of the glass laser. The signals at $2\omega_1-\omega_2$ are detected by 1P28 photomultipliers labeled PMT. Neutral density (or ND) filters attenuate the resonant signal. The Spex 1700 spectrometer which verified the laser frequency is not shown.

plate resonant reflector pumped a continuously tuneable narrow-band dye laser.[5] The effective resolution of the experiment was 2 cm^{-1}, half of which resulted from a periodic tuning error in the dye laser frequency. A portion of the outputs of the dye laser and second-harmonic-generation (SHG) crystal was focused into a diamond sample and another portion into a LiF crystal which served as a reference. Light emitted at the correct angle and frequency (selected by a pair of double monochromators) was detected by 1P28 photomultipliers. The output pulses of the photomultipliers were photographed and measured on the face of a dual-beam oscilloscope.

Since there are two independent components of the third-order susceptibility of a cubic crystal, two polarization conditions were investigated.[1] In one case the beams were polarized along the [110] axis and propagated within a few degrees of the $[1\bar{1}1]$ direction in a 0.9-mm-thick crystal. In the other case the beams propagated along the [110] direction in a 2.2-mm-long crystal. The electric fields were then polarized either along [001] or at a definite angle to that axis. The power level at the crystals was roughly 200 MW/cm^2 for the SHG beam and 40 MW/cm^2 for the dye beam.

An angle of a few degrees between the dye and SHG beams results in a coherence length longer than the sample thickness for the entire region of the resonance. Furthermore, the ω_3 beam can then be separated by spatial filtering. The rejection ratio of the laser beams by the detection apparatus was better than $10^{16}:1$. An analyzer at the monochromator entrance slit defined the polarization direction of the generated wave.

The dynamic range of the detection system was extended by using calibrated neutral-density (ND) filters to attenuate the beam from the sample. The relative signal was computed by taking the ratio of the pulse heights in the signal and reference channels and multiplying by the appropriate filter factor. At least four shots were taken at each setting of the dye laser frequency; the logarithms of the relative signals were then averaged to give the points plotted in Fig. 2. Error bars for typical points were estimated by taking the standard deviation of the logarithms.

The Raman-active optical phonon of frequency ω_R and wave number near $k=0$ is driven by force terms quadratic in the electric fields according to the equation

$$M\ddot{Q}_\sigma + 2M\Gamma_\sigma \dot{Q}_\sigma + M\omega_\sigma^2 Q_\sigma = \sum_{kl} \alpha_{kl}^{(1)}(\sigma) E_k(\omega_1) E_l(-\omega_2) \ . \tag{1}$$

Here Q_σ is the normal coordinate for the mode of frequency ω_σ, M is the effective mass of the atoms in a unit cell, Γ_σ is the half-width at half-maximum of the Raman line, and $\alpha_{ij}^{(1)}(\sigma)$ is the usual Raman polarizability tensor of the σth mode. The driven phonon mode modulates the linear electronic polarizability via this same factor $\alpha_{ij}^{(1)}(\sigma)$:

$$\delta\chi_{ij} = N \sum_\sigma \alpha_{ij}^{(1)}(\sigma) Q_\sigma$$

$$= \frac{N}{M} \sum_{kl\sigma} \frac{\alpha_{ij}^{(1)}(\sigma)\alpha_{lk}^{(1)}(\sigma) E_k(\omega_1) E_l(-\omega_2)}{\omega_\sigma^2 - (\omega_1-\omega_2)^2 + 2i\Gamma_\sigma(\omega_1-\omega_2)} \ , \tag{2}$$

where N is the number of unit cells per unit volume. Accordingly, this modulation of the linear polarizability by the optical phonon provides a contribution to the polarization cubic in the electric fields. Another contribution to the third-order nonlinear susceptibilities arises from electronic transitions with the lattice held fixed. If the material is transparent at ω_1, ω_2, and ω_3 and there is no two-photon absorption at $2\omega_1$, this term is merely a real constant,[1] which will be denoted by $\chi_{ijkl}^{(3)E}$.

Thus in the region of a Raman resonance of a material, the components of the third-order nonlinear susceptibility have the general form

$$\chi_{ijkl}^{(3)E}(-\omega_3, \omega_1, \omega_1, -\omega_2)$$

$$= \chi_{ijkl}^{(3)E} + \frac{N}{6M} \sum_\sigma \left(\frac{\alpha_{ij}^{(1)}(\sigma)\alpha_{kl}^{(1)}(\sigma) + \alpha_{ik}^{(1)}(\sigma)\alpha_{lj}^{(1)}(\sigma)}{\omega_\sigma^2 - (\omega_1-\omega_2)^2 + 2i\Gamma_\sigma(\omega_1-\omega_2)} \right), \tag{3}$$

where terms of order $(\omega_\sigma/\omega_1)^2$ or higher have been neglected and an appropriate numerical factor is introduced to account for the frequency degeneracy.[1] In diamond-type lattices there are three degenerate Raman-active modes with frequency ω_R and width Γ_R. Two independent components of $\chi_{ijkl}^{(3)E}$ ($\chi_{xxxx}^{(3)E}$ and $\chi_{xyxy}^{(3)E}$) and one independent component of $\alpha_{ij}^{(1)}(\sigma)$ (denoted $\alpha_{xy,z}^{(1)}$) do not vanish. Hence from Eq. (3), the relevant nonlinear susceptibilities are

$$\chi_{xxxx}^{(3)}(-\omega_3, \omega_1, \omega_1, -\omega_2) = \chi_{xxxx}^{(3)E} \ ,$$

$$\chi_{xyxy}^{(3)}(-\omega_3, \omega_1, \omega_1, -\omega_2) = \chi_{xyxy}^{(3)E} + \frac{N}{6} \frac{\alpha_{xy,z}^{(1)2}}{M[\omega_R^2 - (\omega_1-\omega_2)^2 + 2i\Gamma_R(\omega_1-\omega_2)]} \ ,$$

$$\chi_{xyxy}^{(3)}(-\omega_3, \omega_1, -\omega_2, \omega_1) = \chi_{xyxy}^{(3)E} + \frac{N}{3} \frac{\alpha_{xy,z}^{(1)2}}{M[\omega_R^2 - (\omega_1-\omega_2)^2 + 2i\Gamma_R(\omega_1-\omega_2)]} \ . \tag{4}$$

With all the electric fields along a [110] direction in diamond, the nonlinear polarization at frequency $\omega_3 = 2\omega_1 - \omega_2$ has the form

$$P_x^{\mathrm{NL}} = P_y^{\mathrm{NL}} = \left(\chi_{[110]}^{(3)E} + \chi_{[110]}^{(3)R} \frac{\Gamma_R}{\omega_R - (\omega_1-\omega_2) + i\Gamma_R} \right)$$

$$\times \frac{E^2(\omega_1)}{2} E_x(-\omega_2) , \quad (5)$$

where

$$\chi^{(3)E}_{[110]} = 3(\chi^{(3)E}_{xxxx} + 3\chi^{(3)E}_{xyxy})$$

and

$$\chi^{(3)R}_{[110]} = \frac{N\alpha^{(1)2}_{xy,z}}{M\omega_R \Gamma_R}$$

When the fields are along the [001] direction, the nonlinear susceptibility is constant:

$$P^{\mathrm{NL}}_x = 3\chi^{(3)E}_{xxxx} E^2_x(\omega_1) E_x(-\omega_2) . \quad (6)$$

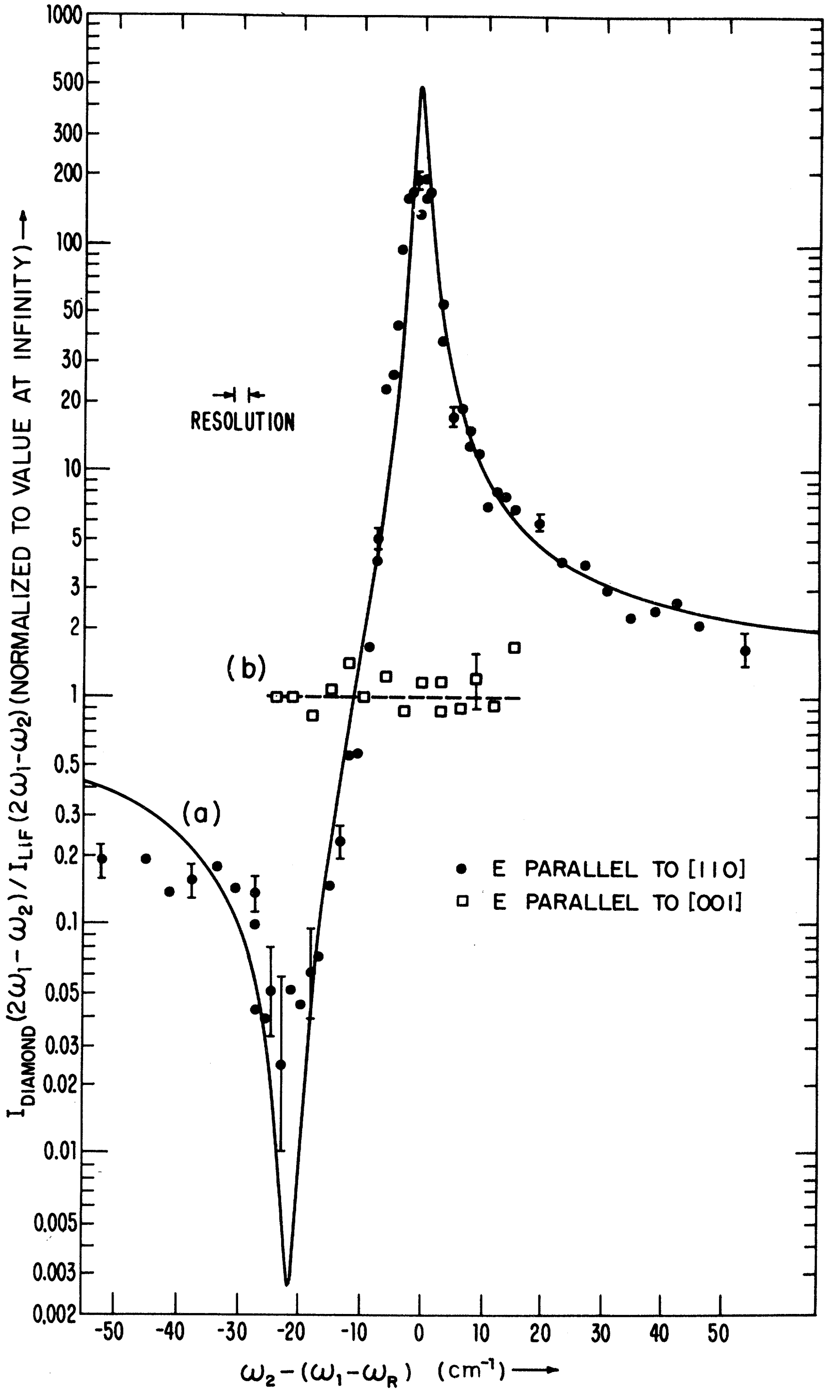

FIG. 2. (a) Relative three-wave mixing intensity in diamond in the region of the optical-phonon frequency for the electric fields polarized along the [100] direction. The solid line is calculated from Eq. (6) with parameters $\Gamma_R = 1.02$ cm^{-1}, $\chi^{(3)R}_{[110]}/\chi^{(3)E}_{[110]} = 21$. (b) Relative intensity for the electric fields polarized along [001]. In both cases the ratio of the intensities from the sample and reference crystals was normalized to its value far from the resonance.

The intensity of the wave generated at $2\omega_1 - \omega_2$ is proportional to the absolute square of the nonlinear susceptibility. In the case of [110] polarization this quantity becomes

$$I(2\omega_1 - \omega_2) \propto (\chi^{(3)E}_{[110]})^2$$

$$\times \frac{\{(\omega_1 - \omega_2) - [\omega_R + (\chi^{(3)R}_{[110]}/\chi^{(3)E}_{[110]})\Gamma_R]\}^2 + \Gamma_R^2}{[(\omega_1 - \omega_2) - \omega_R]^2 + \Gamma_R^2} . \quad (7)$$

If $|\chi^{(3)R}_{[110]}/\chi^{(3)E}_{[110]}| \gg 1$ there is a maximum in the intensity when $\omega_1 - \omega_2 = \omega_R = 1332\ \mathrm{cm}^{-1}$ and a minimum when $\omega_1 - \omega_2 = \omega_R + (\chi^{(3)R}_{[110]}/\chi^{(3)E}_{[110]})\Gamma_R$. The minimum arises physically from a cancellation of the electronic term by the real part of the Raman susceptibility. One such cancellation occurs for $\omega_1 - \omega_2$ very near ω_R but cannot be observed because in that region the three-wave mixing is mostly due to the imaginary part of $\chi^{(3)}$. The other interference is displaced from resonance by several linewidths; the imaginary part is then quite small and a clear minimum results. Since the Raman susceptibility and linewidth of diamond are known,[6,7] a measurement of the frequency separation between the maximum and minimum permits a determination of the electronic nonlinear susceptibility—both in sign and magnitude—without the uncertainties of other methods.

Figure 2(a) is a plot of our data for the [110] polarization along with a theoretical curve of the form in Eq. (7) with $\chi^{(3)R}_{[110]}/\chi^{(3)E}_{[110]} = 21$. The main deviations from theory occur near the peak where the photomultiplier response is nonlinear and near the minimum where a background due to spontaneous anti-Stokes Raman scattering is comparable to the coherent three-wave mixing signal. In spite of these experimental problems with the magnitudes of the maximum and minimum signals, their frequency separation determines a value of the ratio $\chi^{(3)R}_{[110]}/\chi^{(3)E}_{[110]} = 21 \pm 3$ with a precision of 15%. Since the Raman susceptibility is known to be $(3.0 \pm 0.45) \times 10^{-11}\ \mathrm{cm}^3/\mathrm{erg}$, this implies a value of the electronic nonlinear susceptibility of $\chi^{(3)E}_{[110]} = (1.4 \pm 0.4) \times 10^{-12}\ \mathrm{cm}^3/\mathrm{erg}$. A previous measurement of the ratio of the third-harmonic power generated in diamond to that in LiF has given a value of $(0.96 \pm 0.12) \times 10^{-12}\ \mathrm{cm}^3/\mathrm{erg}$.[8] For comparison, a theoretical prediction based on the Unsold approximation yields $0.5 \times 10^{-12}\ \mathrm{cm}^3/\mathrm{erg}$.

No resonance in the intensity of the generated wave appears in Fig. 2(b) when the electric fields all lie in the [001] direction in agreement with Eq. (6). However, a slight rotation of the crystal around the [110] axis results in a marked increase in the intensity at resonance, qualitatively as theory would predict.

Since Eq. (4) shows that $\chi^{(3)\prime}_{\mathrm{RAMAN}}(2\omega_1 - \omega_2) > 0$ for $\omega_1 - \omega_2 < \omega_R$ and $\chi^{(3)\prime}_{\mathrm{RAMAN}}(2\omega_1 - \omega_2) < 0$ for $\omega_1 - \omega_2 > \omega_R$ the sign of $\chi^{(3)E}$ can be assigned absolutely. Also, since the Raman polarizability can be determined from the linear spontaneous Raman-scattering cross section, the magnitude of $\chi^{(3)E}$ can be measured without need of a separate standard. Such data will make detailed quantitative tests of theoretical predictions possible. Both theory and experiment can be extended to polar crystals (e.g., $\mathrm{CaF_2}$ type), to those lacking inversion symmetry[9] (e.g., GaP type), and to crystals of lower symmetry than cubic. Such investigations are currently in progress.

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