OPTICAL HARMONIC GENERATION IN SEMICONDUCTORS AND IN DIELECTRICS CLOSE TO AN ABSORPTION BAND EDGE

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The production of second harmonics in CdS crystals is explained. Near the edge of the absorption band, absorption and also production of second harmonics increase, the source of the latter being a strong electromagnetic wave at the fundamental frequency. It is shown that in this case both processes depend on the frequency in an identical manner. Thus the resulting intensity of the second harmonic, which depends on competition between absorption and production processes, does not change significantly. Results of analysis of a similar effect in third harmonic production in a gas are presented.

1. Second harmonic generation has recently been observed[1] by passing light of energy $\hbar\omega = 1.17$ eV (produced by a $CaWO_4$-Nd^{3+} laser) through a CdS crystal in the temperature range 20 to 300°C. This crystal is interesting since its absorption band Δ is close to $2\hbar\omega$ and depends on the temperature in such a way that $\Delta > 2\hbar\omega$ when $T < T_0$ (T_0 about 235°C), whereas $\Delta < 2\hbar\omega$ for $T > T_0$. The CdS crystal is therefore transparent to the second harmonic if $T < T_0$ and is strongly absorbing if $T > T_0$. Nevertheless it was shown in[1] that the intensity of second harmonic generation does not change significantly on going through the point $T = T_0$.

This result was unexpected; moreover, Kleinman had earlier predicted[2] that the efficiency of second harmonic production would be small in a region where the harmonic was absorbed. On the other hand, Lax et al.[3] have predicted that as the quantity $2\hbar\omega$ approaches the edge of the absorption band Δ, second harmonic generation should go to infinity as $(\Delta - 2\hbar\omega)^{-1/2}$. This result is in error. As was shown by Loudon[4], the rate of second harmonic generation at $\Delta = 2\hbar\omega$ is finite; however its derivative with respect to ω diverges, and hence one might expect a sharp increase in second harmonic generation at this point.

The present paper deals with the generation of second harmonics close to the edge of the absorption band. It is clear from the above discussion that there are two competing processes which together determine the rate of second harmonic generation. On the one hand, as $\Delta \to 2\hbar\omega$ there occurs a sharp increase in the absorption coefficient. On the other hand, there is also a sharp increase in the nonlinear polarizability responsible for second harmonic generation. Therefore the variation in the second harmonic generation with temperature in the region under consideration is determined by the detailed properties of the material medium. Depending on which of the competing processes predominates, one may expect either an increase or a decrease in second harmonic generation. In particular, in cadmium sulphide one might expect that the increase in the absorption coefficient is compensated by a corresponding increase in the nonlinear polarizability, leading to a relatively weak temperature dependence of second harmonic generation in the region T close to T_0.

Since the calculation of these two coefficients for CdS is very difficult, we have analyzed the analogous problem in a gas, where the absorption coefficient and the nonlinear polarizability can be computed exactly. The present calculation shows that in a gas there is complete compensation between the two processes and therefore that the second harmonic generation does not depend on the temperature.

2. In weakly nonlinear media the relation between the dielectric polarization $\mathbf{P}(t)$ and the electric field $\mathbf{E}(t)$ is given by

$$P_\alpha(t) = \int_{-\infty}^{\infty} d\omega e^{-i\omega t}\left\{\chi_{\alpha\beta}^{(1)}(\omega)E_\beta(\omega) + \int_{-\infty}^{\infty} d\omega' \chi_{\alpha\beta\gamma}(\omega', \omega-\omega') \times E_\beta(\omega')E_\gamma(\omega-\omega')\right\}, \quad (1)$$

where $\chi_{\alpha\beta}^{(1)}$ and $\chi_{\alpha\beta\gamma}^{(2)}$ are the first and second order dielectric polarizability tensors respectively, and

where $E_\alpha(\omega)$ are the Fourier components of the electric field.

The nonlinear relationship between $\mathbf{P}(t)$ and $\mathbf{E}(t)$ gives rise to the phenomenon of second harmonic generation. We limit ourselves to the case in which the second harmonic intensity is small compared to the intensity of the fundamental, so that the latter field is described by the equation

$$\Delta E_\alpha^{(1)} + \omega^2 c^{-2}[\delta_{\alpha\beta} + \chi_{\alpha\beta}^{(1)}(\omega)]E_\beta^{(1)} = 0, \qquad (2)$$

where $E_\alpha^{(1)}$ is the amplitude of the α-th component of the electric field at the fundamental. Then the equation describing second harmonic generation has the form

$$\Delta E_\alpha^{(2)} + 4\omega^2 c^{-2}[\delta_{\alpha\beta} + \chi_{\alpha\beta}^{(1)}(2\omega)]E_\beta^{(2)} + 2\omega^2 c^{-2}\chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega)E_\beta^{(1)}E_\gamma^{(1)} = 0, \qquad (3)$$

where $E_\alpha^{(2)}$ are the components of the second harmonic electric field.

For the tensors $\chi_{\alpha\beta}^{(1)}$ and $\chi_{\alpha\beta\gamma}^{(2)}$ one may obtain the following expressions (cf. for example [5]):

$$\chi_{\alpha\beta}^{(1)}(\omega) = \frac{4\pi}{\hbar}\sum_{n,m}\rho_n\left[\frac{P_{nm}^\beta P_{mn}^\alpha}{\omega + \omega_{mn}} + \frac{P_{nm}^\alpha P_{mn}^\beta}{\omega_{mn} - \omega}\right], \qquad (4)$$

$$\chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega) = \frac{2\pi}{\hbar}\sum_{n,m,l}\rho_n\left[\frac{P_{nm}^\alpha P_{ml}^\beta P_{ln}^\gamma + P_{nm}^\alpha P_{ml}^\gamma P_{ln}^\beta}{(2\omega - \omega_{mn})(\omega - \omega_{ln})} + \frac{P_{nm}^\beta P_{ml}^\alpha P_{ln}^\gamma + P_{nm}^\gamma P_{ml}^\alpha P_{ln}^\beta}{(\omega + \omega_{mn})(\omega - \omega_{ln})} + \frac{P_{nm}^\beta P_{ml}^\gamma P_{ln}^\alpha + P_{nm}^\gamma P_{ml}^\beta P_{ln}^\alpha}{(\omega + \omega_{mn})(2\omega + \omega_{ln})}\right], \qquad (5)$$

Here ρ_n is a diagonal element of the equilibrium density matrix, P_{mn}^α is the matrix element of the α-th component of the dipole moment per unit volume of the medium; $\omega_{mn} = (\mathscr{E}_m - \mathscr{E}_n)/\hbar$, the $\mathscr{E}_n$ are the energy levels of the medium. The quantities $1/(\omega \pm \omega_{mn})$ should be understood as the limit $\lim_{\Gamma \to 0}[1/(\omega \pm \omega_{mn}) + i\Gamma]$. In a semiconductor the energy levels are characterized by two quantum numbers $(s, \mathbf{k})$ where s is the zone number and $\mathbf{k}$ is the quasi-momentum of the electron. Because of the conservation of quasi-momentum, the matrix element of the dipole moment operator may be written

$$P_{nn}^x = P_{s\mathbf{k}, s'\mathbf{k}'}^x = P_{ss'}^x(\mathbf{k})\delta_{\mathbf{k}\mathbf{k}'}. \qquad (6)$$

We assume that the energy spectra of the valence band $\mathscr{E}_0(\mathbf{k})$ and of the conduction band $\mathscr{E}_1(\mathbf{k})$ close to the point $\mathbf{k} = 0$ have the form

$$\mathscr{E}_0(\mathbf{k}) = -\hbar^2\mathbf{k}^2/2m_0, \quad \mathscr{E}_1(\mathbf{k}) = \Delta(T) + \hbar^2\mathbf{k}^2/2m_1, \qquad (7)$$

where m_0 and m_1 are the effective masses of the charge carriers in the valence and conduction bands respectively and where $\Delta(T)$ is the width of the forbidden band. Further let $kT \ll \Delta$, whence only the valence band is occupied. Keeping those terms in (4) and (5) which give the largest contribution in the case where $\Delta(T)$ is close to $2\hbar\omega$, we obtain

$$\chi_{\alpha\beta}^{(1)}(2\omega) = 4\pi\sum_k \frac{P_{01}^\alpha(\mathbf{k})P_{10}^\beta(\mathbf{k})}{\Delta - 2\hbar\omega + \hbar^2\mathbf{k}^2/2\mu},$$

$$\chi_{\alpha\beta\gamma}^{(2)}(\omega, \omega) = 2\pi\sum_k \frac{P_{01}^\alpha(\mathbf{k})F_{10}^{\beta\gamma}(\mathbf{k})}{\Delta - 2\hbar\omega + \hbar^2\mathbf{k}^2/2\mu},$$

$$F_{10}^{\beta\gamma}(\mathbf{k}) = \sum_s \frac{P_{1s}^\beta(\mathbf{k})P_{s0}^\gamma(\mathbf{k}) + P_{1s}^\gamma(\mathbf{k})P_{s0}^\beta(\mathbf{k})}{\omega_{s0} - \omega}, \qquad (8)$$

where $\mu^{-1} = m_0^{-1} + m_1^{-1}$. It is clear from (4) and (8) that

$$\chi_{\alpha\beta}^{(1)}(2\omega) \gg \chi_{\alpha\beta}^{(1)}(\omega). \qquad (9)$$

3. Consider a plate of thickness a on which a strong monochromatic plane wave of frequency ω is incident normally. We assume that the wave is linearly polarized and hence that its electric vector is parallel to the plane of the plate. We assume the plate to be uniform, nonmagnetic, and optically inactive, so that its dielectric polarization is given by expression (1). If the plate is transparent to frequency ω it is simple to show, by solving (2) and (3), that after traversing the plate the intensity in the second harmonic $J(2\omega)$, propagating in the same direction as the fundamental, is given by the expression

$$J(2\omega) = {}^1\!/_4 J(\omega)A^2(2\omega)\,|1 - \exp[i(2k_1 - k_2)a]|^2 \times \exp[-2\mathrm{Im}\,k_2 a], \qquad (10)$$

where

$$A(2\omega) = |\chi^{(2)}(\omega, \omega)E^{(1)}/[\chi^{(1)}(2\omega) - \chi^{(1)}(\omega)]|,$$

$$k_1 = [1 + \chi^{(1)}(\omega)]^{1/2}\omega/c, \quad k_2 = [1 + \chi^{(1)}(2\omega)]^{1/2}2\omega/c; \qquad (11)$$

$\chi^{(1)}$ and $\chi^{(2)}$ are to be understood as the diagonal elements of the corresponding tensors, and $J(\omega)$ is the intensity of the fundamental.

If the plate is also transparent to frequency 2ω, i.e., $\mathrm{Im}\,k_2 a \ll 1$ then (10) takes the form

$$J(2\omega) = J(\omega)A^2(2\omega)\sin^2[(2k_1 - k_2)a/2]. \qquad (12)$$

For small thicknesses or for the case of small phase mismatch, i.e., when $|(2k_1 - k_2)a| \ll 1$, we have, using (10),

$$J(2\omega) = 4J(\omega)\,|\chi^{(2)}(\omega, \omega)E^{(1)}|^2[\omega^2 a/c^2(2k_1 + k_2)]^2. \qquad (13)$$

It is clear from (12) that the intensity of the second harmonic oscillates as a function of the parameter $(2k_1 - k_2)a$, which may vary either due to a change

in the thickness or due to the temperature dependence of the difference $2k_1 - k_2$.

If the plate is transparent to ω but opaque to 2ω, i.e., if Im $(2k_1 - k_2)a \gg 1$, then (10) takes the form

$$J(2\omega) = J(\omega)A^2(2\omega)/4. \quad (14)$$

From this equation it follows that the second harmonic intensity is independent of the plate thickness.

4. We now analyze the experiments on second harmonic generation in CdS. In the temperature range 20—120°C, Miller et al.[1] observed oscillations in the second harmonic intensity. Since the CdS crystal is transparent to both the fundamental and second harmonic in this temperature region, it was natural to conclude that the observed oscillations were described by expression (12), so that second harmonic generation is described by the coefficient $A(2\omega)$. However, it follows from (14) that the coefficient $A(2\omega)$ also determines the second harmonic intensity when the crystal is strongly absorbing. As the temperature is varied near T_0, we can simplify the expression for the coefficient $A(2\omega)$ according to formula (9) and we obtain

$$A(2\omega) = |\chi^{(2)}(\omega, \omega)E^{(1)}/\chi^{(1)}(2\omega)|. \quad (15)$$

As is clear from (8), $\chi^{(1)}(2\omega)$ and $\chi^{(2)}(\omega, \omega)$ vary appreciably in the region close to T_0, because of the sharp decrease in the denominators at this point. However the intensity of second harmonic generation is determined by their ratio (15), so that we can expect a weak dependence of $J(2\omega)$ on the temperature; this is, in fact, in agreement with experimental data. For a thin crystal we note that according to expression (13) $J(2\omega)$ should increase strongly as T approaches T_0, owing to the rapid increase in $\chi^{(2)}$. Detailed calculation of $\chi^{(1)}$ and $\chi^{(2)}$ does not seem possible at present because of insufficient information on the structure of the energy bands and the wave functions of the electrons in CdS.

5. It is of interest to consider generation of odd harmonics in a gas; this process can be calculated completely and the corresponding polarizability coefficients obtained. If the frequency of the odd harmonic is close to one of the natural frequencies of the atom, then by changing the temperature of the gas and hence the Doppler width of the atomic levels, one may strongly effect the absorption coefficient of the odd harmonic and the corresponding nonlinear polarizability. At the same time, according to the ideas in Sec. 4, the rate of generation of the odd harmonic should not change very markedly.

We will show this as follows. Since second harmonic generation is impossible in a gas, which is an isotropic medium, we consider third harmonic generation. The equation describing the formation of the third harmonic is similar to (3). It can be shown easily that the intensity of the third harmonic will be given by expressions (10)—(14) if k_2 is changed to $k_3 = [1 + \chi^{(1)}(3\omega)]^{1/2}3\omega/c$, and if the coefficient $A(2\omega)$ is changed to the coefficient $A(3\omega)$, which has the form

$$A(3\omega) = (1/2)|\chi^{(3)}(\omega, \omega, \omega)(E^{(1)})^2/[\chi^{(1)}(3\omega) - \chi^{(1)}(\omega)]|, \quad (16)$$

where $\chi^{(3)}(\omega, \omega, \omega)$ is the coefficient of third order polarizability[5].

If the frequency ω satisfies the inequality

$$3\omega - \omega_0 \ll \omega_0, \quad (17)$$

where ω_0 is an atomic transition frequency, then in the temperature range $kT \ll \hbar\omega$ we will have the following expressions for the first and third order polarizability coefficients:

$$\chi^{(1)}(3\omega) = -\gamma Nc(m/kT)^{1/2}I_+[(3\omega - \omega_0)c/\omega_0(kT/m)^{1/2}],$$

$$\chi^{(3)}(\omega, \omega, \omega) = -\delta Nc(m/kT)^{1/2}I_+[(3\omega - \omega_0)c/\omega_0(kT/m)^{1/2}], \quad (18)$$

where γ and δ are certain temperature-independent constants, N is the number of atoms per unit volume, c is the velocity of light and

$$I_+(\beta) = \int_{-\infty}^{\infty} \frac{e^{-x^2/2}\,dx}{\beta - x}. \quad (19)$$

In the two limiting cases $I_+(\beta)$ has the form

$$I_+(\beta) = \begin{cases} \beta\sqrt{2\pi} - i\pi, & |\beta| \ll 1, \quad \operatorname{Im}\beta > 0 \\ \beta^{-1}\sqrt{2\pi} - i\pi e^{-\beta^2/2}, & |\beta| \gg 1, \quad \operatorname{Im}\beta > 0 \end{cases}. \quad (20)$$

It follows therefore from (18)—(20) that $\chi^{(1)}(3\omega)$ depends strongly on the temperature, especially Im $\chi^{(1)}(3\omega)$. This means that by varying the temperature we may sharply increase the third harmonic absorption. Moreover $\chi^{(3)}(\omega, \omega, \omega)$ increases with increasing temperature for the same reasons as does $\chi^{(1)}(3\omega)$. Nevertheless the intensity of the third harmonic is independent of temperature, as may be seen from (16) and (18).

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