NONLINEAR INTERBAND AND PLASMA EFFECTS IN SOLIDS

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The theoretical analysis of the optical harmonics in quartz as reported by Franken and collaborators[1] was based on a phenomenological approach. In order to optimize the experimental performance of various crystals we have developed a semiclassical theory which takes into account not only the symmetry of the crystal but a simple representation of its band properties as well. In the absence of a center of symmetry as in a piezoelectric crystal the nonlinear motion of the bound electron, which is responsible for the radiation, can be represented by the following simple equation:

$$\ddot{x}+\omega_0^2 x+\alpha x^2=(eE/m)e^{j\omega t}, \tag{1}$$

where ω_0 is the oscillator frequency, αx^2 is the asymmetrical nonlinear force term and $Ee^{j\omega t}$ is the large driving electric field of the optical maser. If the displacement x is represented in a Fourier expansion, the first order term x_1 represents the dispersion and the second order term,

$$x_2 \approx -\frac{\alpha e^2 E^2}{m^2(\omega_0^2-\omega^2)^2(\omega_0^2-4\omega^2)}, \tag{2}$$

is the harmonic component of the displacement. In our theory we assume that each electron in the crystal behaves as a classical radiator in which the radiated power $P=(2e^2/3c^3)(\ddot{x})^2$, and that the oscillator frequencies are distributed over the bands. Only the allowed direct transitions give large dispersion and therefore account principally for the phenomenon observed. Then since $x_2 \sim x_1^2 \sim f^2 \sim M^4/\omega_0^2$, where f is the oscillator strength and M is the momentum matrix element for the allowed transition, we can write the power as proportional to the following integral:

$$P_2 \sim \frac{2e^2}{3c^3}\int_0^{p_{\max}} (\ddot{x})^2 d^3p \sim \int_0^{p_{\max}} \frac{(\omega_0-\omega_g)dp}{\omega_0^2(\omega_0^2-\omega^2)^4(\omega_0^2-4\omega^2)^2}, \tag{3}$$

where $\omega_0=\omega_g+p^2/2\mu\hbar$ and $1/\mu=1/m_v+1/m_c$ for simple parabolic bands; ω_g is the frequency corresponding to the energy gap, p is the momentum, and m_v and m_c are the effective masses of the electron in the valence and conduction bands, respectively. For harmonic doubling it is necessary that $\omega<\omega_g/2$. Hence $\omega_0^2 \gg \omega^2$ which allows an approximate evaluation of the integral of Eq. (3) to give the following result, if we take $p_{\max}$ large in Eq. (3):

$$P_2 \approx C_2\left[\frac{(2/3-\omega/\omega_g)}{(1/2-\omega/\omega_g)^{1/2}}+\frac{(2/3+\omega/\omega_g)}{(1/2+\omega/\omega_g)^{1/2}}-\tfrac{4}{3}\sqrt{2}\right], \tag{4}$$

where

$$C_2=48\pi a^3 e^6 E^4 M^4 \alpha^2 \sqrt{\omega_g}/h^3 c^3 m_v^4 \langle\omega_0^9\rangle_{\mathrm{av}}(\mu\hbar)^{1/2},$$

and a is the lattice constant. We have plotted this function in Fig. 1, and it is apparent from the results and Eq. (4) that although the oscillators are distributed over the band the singularity for $\omega/\omega_g=1/2$ is still retained but is not as strong as that for a single oscillator.

To test this theory qualitatively we have examined a number of piezoelectric and ferroelectric materials[2] and observed the magnitude of the second harmonic output as stimulated by a ruby laser focused under analogous geometric conditions so that the geometrical factor[3] of the crystalline array was essentially the same for all these samples. For comparison the relative intensity of three of these, SiO_2, Al_2O_3, and ZnS, are plotted in Fig. 1 as a function of the parameter ω/ω_g. In this figure we have taken the out-

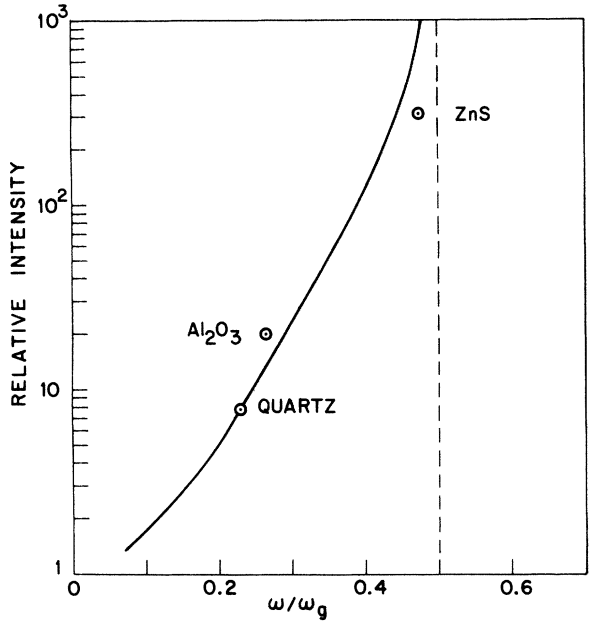

FIG. 1. Comparison of experimentally measured second harmonic generation from quartz, Al_2O_3, and ZnS with theory. The theoretical curve is adjusted to pass through the quartz experimental point.

put of quartz on the theoretical curve. As expected from the theory, ZnS, which has an energy gap just above the second harmonic, turned out to be the most efficient frequency doubler. Its output, however, falls below the theoretical curve. This is not surprising since the nonlinear coefficient α probably differs for these three crystals and if the piezoelectric effect is a measure of this coefficient, the α of ZnS should be smaller. Furthermore the matrix elements for the interband transition, the mass values, and the mean oscillator frequencies may also be somewhat different for these materials.

Our analysis in principle also applies to the surface layers of a cubic crystal or that of isotropic materials, in that for the first few atomic layers the crystalline potential in the direction perpendicular to the surface is no longer symmetrical and therefore should exhibit nonlinear second harmonic generation. In this case the concept of the band structure is probably not applicable and a model intermediate between the single-electron model and that for the bulk has to be developed. Nevertheless experimental observations of the surface phenomenon on diamond and glass have been observed.[2] However, no attempt has been made to compare the results with theory. Quantitative measurements of surface effects should provide information about the binding of electrons in this region and the onset of breakdown phenomena should determine effective energy gaps for surface layers as optical masers of different wavelengths become available.

In a manner analogous to the above treatment for the second harmonic we carried out calculations for the third harmonic which would be observable in cubic crystals with a high-energy gap such as diamond and the alkali halides by replacing the asymmetrical nonlinear force term in Eq. (1) by βx^3. The integral to be evaluated is now

$$P_3 \sim \int_0^{p_{\max}} \frac{(\omega_0 - \omega_g)dp}{\omega_0^2(\omega_0^2-\omega^2)^6(\omega_0^2-9\omega^2)^2}. \qquad (5)$$

Assuming that $\omega < \omega_g/3$ the final result is

$$P_3 \approx C_3\left[\frac{(4/9-\omega/\omega_g)}{(1/3-\omega/\omega_g)^{1/2}} + \frac{(4/9+\omega/\omega_g)}{(1/3+\omega/\omega_g)^{1/2}} - \tfrac{8}{9}\sqrt{3}\right], \qquad (6)$$

where

$$C_3 = 16(\sqrt{6})\pi a^3 e^8 E^6 M^4 \beta^2 \sqrt{\omega_g}/h^3 c^3 m_v{}^6 \langle \omega_0{}^{13} \rangle_{\mathrm{av}} (\mu\hbar)^{1/2}$$

It is evident that the most efficient harmonic tripling will be obtained with a material in which the direct energy gap is just a little larger than three times the output frequency of the laser. Thus for the ruby laser, diamond and the alkali halides of the iodide series would be most promising.

We have also evaluated the mixing of frequencies, using an equation for the asymmetrical oscillator similar to Eq. (1), in terms of the present model with similar approximations. Considering two incident waves of frequencies ω_1 and ω_2 we obtain a result identical to Eq. (4) except that now ω is replaced by $(\omega_1 \pm \omega_2)/2$. It is apparent that both the sum and difference frequencies are generated and that the condition for proper operation is that $(\omega_1+\omega_2) < \omega_g$; consequently only the sum presents a realistic condition for large amplitude mixing. The power of the difference frequency would be several orders of magnitude below the sum output since on a curve as in Fig. 1 it would occur at low values of the abscissa. The above result suggests that if one of the amplitudes can be made extreme-

ly large, the second need only be of modest value to provide detectable output at the sum frequency. Under proper conditions, one of these sources may be a monochromator in the infrared and the other a ruby laser which would permit generation of visible green light, for example. If the theory is considered for a cubic crystal or an isotropic material in which a large dc or microwave field E_0 of the order of 10^6 volts/cm, just below breakdown, is introduced, then the results analogous to Eq. (4) suggest the possibility of inducing frequency doubling. The result is given by Eq. (4) except that in C_2, α is replaced by $3\beta eE_0/m\omega_0^2$, where the generation is achieved by making E_0 large. Preliminary experiments have shown this effect to occur.[4]

Nonlinear effects in electron plasmas as in a metal can be excited by an optical maser. This was demonstrated experimentally at the edge of a razor blade[4] which emitted second harmonics. In this case the equation of motion can be written in the following form[5]:

$$\frac{d\vec{v}}{dt}=\frac{e\vec{E}_{\text{eff}}}{m}-\int\vec{v}\omega_p^2\,dt, \tag{7}$$

where

$$\vec{v}=\vec{v}_1e^{j\omega t}+\vec{v}_2e^{2j\omega t},$$

$$\omega_p^2=\omega_{p0}^2+\omega_{p1}^2e^{j\omega t},$$

$$E_{\text{eff}}=Ee^{j\omega t}/(1+L\chi_0),$$

$$\omega_p^2=(ne^2/m\epsilon)[L/(1+L\chi_0)];$$

χ_0 is the dielectric susceptibility, $n=n_0+n_1e^{j\omega t}$ is the electron density, and L is the depolarizing factor. From $\operatorname{div}\epsilon_0\vec{E}=n_1e$ we can estimate that $n_1\approx10^{15}/\text{cm}^3$ for $E\approx10^5$ v/cm at $\lambda\approx0.7\,\mu$. Then if we solve the nonlinear Eq. (7) in the appropriate manner for the second harmonic we obtain for the power radiated per electron:

$$P_2=\tfrac{8}{3}\frac{e^4}{c^3}\frac{\omega^4E_{\text{eff}}^2\omega_{p1}^4}{m^2(\omega^2-\omega_{p0}^2)^2(4\omega^2-\omega_{p0}^2)^2}. \tag{8}$$

From Eq. (8) we see that the power radiated can be tremendously enhanced if the metal is selected such that the plasma frequency and maser frequency are related by $\omega=\omega_{p0}$ or $\omega=\omega_{p0}/2$. The effect should be much greater than that in an insulator under these conditions. Furthermore we see that harmonic doubling is possible in an isotropic plasma if polarization effects are induced, i.e., $L\neq0$. Thus we found that on a clean razor edge there are no harmonics generated when $\vec{E}$ is parallel to the surface, but only when $\vec{E}$ is perpendicular to the surface. However, when a large magnetic field is placed parallel to the surface of the metal and $\vec{E}$ transverse to it but still parallel to the surface, the theory shows that nonlinear effects are again induced. Third harmonic generation and mixing by plasmas can be analyzed in a similar manner.

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