treated as delta functions of varying area qA,

$$i(t-t_k)=qA\,\delta(t-t_k)\,, \tag{I18}$$

where q is the charge content of the pulse referred to the first dynode of the photomultiplier, so that $\bar{q}=e$, and A is the gain, one obtains for (I17)

$$\Phi(\omega)=\beta^2e^2A^2\Phi_p(\omega)+\Gamma(\beta\bar{p}e^2A^2/2\pi)\,. \tag{I19}$$

where $\Gamma=\langle q^2\rangle_{\rm av}/\bar{q}^2$. Noting that the anode current is given by

$$I_0=Ae\beta\bar{p}\,, \tag{I20}$$

one can rewrite Eq. (I19) as

$$\Phi(\omega)=I_0(Ae/2\pi)[\Gamma+2\pi\beta\Phi_p(\omega)/\bar{p}]\,. \tag{I21}$$

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Optical Nonlinearities of a Plasma*

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Second-harmonic generation and stimulated Raman effects for a plasma are calculated by the same methods that have been used for bound electrons. The nonlinear susceptibility describing the stimulated Raman effect in a gaseous or metallic plasma is 6 to 10 orders of magnitude smaller than the corresponding effect in liquids. This process in a plasma can also be described as the parametric interaction between a damped plasma wave and two light waves. The second-harmonic generation from a plasma boundary is dominated by a surface term which originates from the discontinuity in the normal component of the electric field. It is shown that the observed second-harmonic generation from metallic silver probably stems from bound ion cores in the surface layer rather than from a plasma surface term.

I. INTRODUCTION

THE basic nonlinearity in the interaction between a free electron and an electromagnetic wave is caused by the Lorentz force. Additional nonlinearities may result from convective density fluctuations in the plasma. The nonlinearities in gaseous plasmas have been studied extensively in the microwave region of the electromagnetic spectrum.[1,2] Recently much attention has been given to optical nonlinearities of a plasma, although they are by their very nature rather small.[3–11] In this paper hydrodynamic terms and convection will be ignored.

The same basic formalism can be used to describe the nonlinearities for bound and free electrons. This is particularly evident in the formulation of Cheng and Miller[5] and of Pine,[12] who emphasized the self-consistent-field description of the nonlinear susceptibilities. In Sec. II of this paper, the second-harmonic volume polarization for a plasma is rederived. The self-consistent-field correction on this longitudinal polarization is explicitly exhibited in the same manner as has been done by Ehrenreich and Cohen[13] for the longitudinal linear dielectric constant. In Sec. III, it is shown that surface terms are actually more important than the volume effect for the second-harmonic generation (SHG) from a metallic surface. Jha[14] has first called attention to these plasma surface terms. Our results are somewhat different from Jha's and in better agreement with recent experimental observations. We show furthermore that the dominant contribution to the SHG may come from bound electrons in the ion cores at the surface rather than from the conduction electrons.

The next higher order nonlinearity describes the Raman-type effects in a plasma. If, for example, a laser beam at frequency ω_L is incident on a plasma, the plasma will present exponential gain for a light beam

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at $\omega_s=\omega_L-\omega_{p,q_L-q_s}$ where ω_{p,q_L-q_s} is the frequency of a plasma wave with wave vector $\mathbf{q}_L-\mathbf{q}_s$. If both beams at ω_L and ω_s are incident, generation of the antistokes frequency at $2\omega_L-\omega_s$ is possible, etc. All these effects are derived in a straightforward manner in Sec. IV by a simple extension of the SHG calculation of Sec. II. The same numerical results are obtained as from more complex calculations.[7–11] The stimulated Raman effect is so small that it will be of little use as a probe for gaseous plasmas, although the Raman-type nonlinearity may be important in semiconductor plasmas in the far infrared. In Sec. V the same Raman effect is described as the parametric interaction between two light waves and a plasma wave. This illustrates again the parallel treatment for free and bound electrons. The Raman effect in a plasma is quite analogous to the Raman effect in liquids and solids,[15] if the optical phonons are replaced by plasmons.

II. SELF-CONSISTENT-FIELD CALCULATION OF THE LONGITUDINAL SECOND-HARMONIC POLARIZATION IN A PLASMA

General expressions for the lowest order nonlinear susceptibility have been given by Cheng and Miller [Eq. (13) of Ref. 5] and by Pine [Eq. (18) of Ref. 12]. Their results are valid for Bloch one-electron wave functions in a periodic lattice potential and can be specialized for the case of free electrons. Because of the complexity of the expressions, it seems worthwhile to rederive the result for free electrons in a special gauge, which will clearly and explicitly exhibit the self-consistent-field corrections. Ehrenreich and Cohen first utilized this method to get physical insight in the linear self-consistent dielectric constant. They also pointed out that the one-electron Hamiltonian approach is equivalent to the random-phase approximation in the exact many-body problem.

The zero-order or equilibrium density matrix for an ensemble of free electrons with eigenstates,

$$|\mathbf{k}\rangle=\Omega^{-1/2}\exp(i\mathbf{k}\cdot\mathbf{r}),$$

where Ω is a volume of normalization, is given by

$$\rho^{(0)}|\mathbf{k}\rangle=f_0(\epsilon_\mathbf{k})|\mathbf{k}\rangle.$$

Here f_0 is the Fermi-Dirac distribution function and $\epsilon_\mathbf{k}=\hbar^2k^2/2m$ is the unperturbed (kinetic) energy in the state $|\mathbf{k}\rangle$. The equation of motion for the density matrix must now be solved in successive approximation, when the perturbation by the transverse electromagnetic wave and the self-consistent Coulomb screening potential is admitted. Since general expressions have already appeared elsewhere,[16] here only the physically dominant terms will be retained. The perturbation may be written as

$$\mathcal{H}_{\text{pert}}=(e^2/2mc^2)\mathbf{A}^2+e\varphi_s. \quad (1)$$

It can be shown by explicit calculation that for free electrons the contributions from the linear term, $-(e/2mc)\{\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p}\}$, are smaller by a factor $(\hbar\omega/mc^2)$, where ω is the light frequency. The transverse vector potential $\mathbf{A}$ describes the light wave *inside* the plasma. It is *not* the incident field, but the transmitted wave into the plasma,

$$\mathbf{A}=\mathbf{A}_0\exp(i\mathbf{q}\cdot\mathbf{r}-i\omega t)+\mathbf{A}_0^*\exp(-i\mathbf{q}\cdot\mathbf{r}+i\omega t). \quad (2)$$

The complex amplitude $\mathbf{A}_0$ has twice the value of the more conventional definition.

With the perturbation given by Eqs. (1) and (2), the lowest order nonvanishing density-matrix elements at the harmonic frequency 2ω are given by

$$-(2\hbar\omega)\langle\mathbf{k}|\rho^{(2\omega)}|\mathbf{k}-2\mathbf{q}\rangle=(\epsilon_\mathbf{k}-\epsilon_{\mathbf{k}-2\mathbf{q}})\langle\mathbf{k}|\rho^{(2\omega)}|\mathbf{k}-2\mathbf{q}\rangle +\langle\mathbf{k}|(e^2/2mc^2)\mathbf{A}^2+e\varphi_s|\mathbf{k}-2\mathbf{q}\rangle\{f_0(\epsilon_\mathbf{k})-f_0(\epsilon_{\mathbf{k}-2\mathbf{q}})\} +i\Gamma\langle\mathbf{k}|\rho^{(2\omega)}|\mathbf{k}-2\mathbf{q}\rangle. \quad (3)$$

The last term is a phenomenological damping term to represent the effect of collisions and Landau damping. The screening potential is related to the induced charge density by Poisson's equation. Using the Fourier series expansion for the screening potential,

$$\varphi_s(\mathbf{r})=\sum_{\mathbf{q}'}\varphi_{s,\mathbf{q}'}e^{+i\mathbf{q}'\cdot\mathbf{r}},$$

and for the charge density,

$$n^{(2\omega)}e=e\sum_{\mathbf{q}'}e^{+i\mathbf{q}'\cdot\mathbf{r}}\sum_{\mathbf{k}'}\langle k'|\rho^{(2\omega)}|\mathbf{k}'-\mathbf{q}'\rangle,$$

one finds

$$\langle\mathbf{k}|e\varphi_s^{(2\omega)}|\mathbf{k}-2\mathbf{q}\rangle =(4\pi e^2/4q^2)\sum_{k'}\langle k'|\rho^{(2\omega)}|k'-2\mathbf{q}\rangle. \quad (4)$$

When Eq. (4) is substituted back into Eq. (3), the solution can, after some manipulation, be written in the form

$$\langle\mathbf{k}|\rho^{(2\omega)}|\mathbf{k}-2\mathbf{q}\rangle =\frac{f_0(\epsilon_{\mathbf{k}-2\mathbf{q}})-f_0(\epsilon_\mathbf{k})}{\epsilon_{\mathbf{k}-2\mathbf{q}}-\epsilon_\mathbf{k}+2\hbar\omega+i\Gamma}\frac{e^2A_0^2}{2mc^2}\frac{1}{\epsilon_{\text{SCF}}(2\omega,2\mathbf{q})}, \quad (5)$$

where $\epsilon_{\text{SCF}}(2\omega,2\mathbf{q})$ is the longitudinal, frequency- and wave-vector-dependent, self-consistent linear dielectric constant calculated by Ehrenreich and Cohen,

$$\epsilon_{\text{SCF}}(\omega,\mathbf{q})=1-\frac{4\pi e^2}{q^2}\sum_{k'}\frac{f_0(\epsilon_{\mathbf{k}-\mathbf{q}})-f_0(\epsilon_\mathbf{k})}{\epsilon_{\mathbf{k}-\mathbf{q}}-\epsilon_\mathbf{k}+\hbar\omega+i\Gamma}. \quad (6)$$

The Fourier transforms of the current density operator are given by

$$\mathbf{j}^{(0)}(\mathbf{q},0)=(\hbar e/2im)e^{-i\mathbf{q}\cdot\mathbf{r}}(-i\mathbf{q}+2\nabla),$$
$$\mathbf{j}^{(1)}(\mathbf{q},\omega)=-(e^2/mc)\mathbf{A}_0.$$

[15] Y. R. Shen and N. Bloembergen, Phys. Rev. **137**, 1787 (1965).
[16] See, for example, Refs. 5 and 12, or N. Bloembergen, *Nonlinear Optics* (W. A. Benjamin, Inc., New York, 1965).

The expectation value of the nonlinear second-harmonic current density is

$$\langle j(2\omega,2\mathbf{q})\rangle=\sum_{\mathbf{k}}\langle\mathbf{k}-2\mathbf{q}|j^{(0)}|\mathbf{k}\rangle\langle\mathbf{k}|\rho^{(2\omega)}|\mathbf{k}-2\mathbf{q}\rangle = (he/m)\sum_{\mathbf{k}}(\mathbf{k}-\mathbf{q})(\mathbf{k}|\rho^{(2\omega)}|\mathbf{k}-2\mathbf{q}). \quad (7)$$

The nonlinear current density given by Eqs. (5) and (7) creates the second-harmonic field. At optical frequencies the change in electron energy and the damping rate are small compared to the photon energy. If the denominator in Eq. (5) is thus approximated by $2\hbar\omega$, one finds immediately from the relations $\sum\mathbf{k}f(\epsilon_{\mathbf{k}})=0$, $\sum\mathbf{q}f(\epsilon_{\mathbf{k}})=N\mathbf{q}$, where N is the number of electrons per unit volume, that the current density is given by

$$\mathbf{j}^{\mathrm{NL}}(\mathbf{r},t)=[Ne^3\mathbf{q}A_0^2/2m^2\omega c^2\epsilon_{\mathrm{SCF}}(2\omega,2\mathbf{q})]\times\exp(2i\mathbf{q}\cdot\mathbf{r}-2i\omega t).$$

The corresponding nonlinear susceptibility is obtained by replacing $\mathbf{j}(2\omega)$ by $-2i\omega\mathbf{P}(2\omega)$ and the vector potential $\mathbf{A}$ by $(ic/\omega)\mathbf{E}$. One finds

$$\mathbf{P}^{\mathrm{NLS}}=\chi^{\mathrm{NL}}(2\omega):\mathbf{E}^2=[-iNe^3E_0^2\mathbf{q}/4m^2\omega^4\epsilon_{\mathrm{SCF}}(2\omega,2\mathbf{q})]\times\exp(2i\mathbf{q}\cdot\mathbf{r}-2i\omega t). \quad (8)$$

This result for the longitudinal second-harmonic polarization could also have been obtained more directly from the relation that the divergence of this polarization equals the second-harmonic charge density:

$$\operatorname{div}\mathbf{P}(2\omega)=e\sum_{\mathbf{k}}\langle\mathbf{k}|\rho^{(2\omega)}|\mathbf{k}-2\mathbf{q}\rangle$$
$$\mathbf{P}^{\mathrm{NLS}}=[2ie\mathbf{q}/(2q)^2]\sum_{\mathbf{k}}\langle\mathbf{k}|\rho^{(2\omega)}|\mathbf{k}-2\mathbf{q}\rangle.$$

Substitution of Eq. (5) and expansion of its denominator in the approximation, $\hbar^2/2m\{2\mathbf{k}\cdot(2\mathbf{q})+(2\mathbf{q})^2\}\ll 2\hbar\omega$, again yields Eq. (8). In the limit of low electron density, $2\omega\gg\omega_p$ and $\epsilon_{\mathrm{SCF}}\sim 1$, and substituting $q/\omega=c^{-1}$, one fines the same nonlinear susceptibility $(-iNe^3/4m^2c\omega^3)$ as was first found by very elementary considerations.[17] The occurrence of ϵ_{SCF} in the denominator was not explicitly noted before, but its physical origin is evident from the present calculation. Since the polarization is longitudinal there is no second-harmonic power radiated in the plasma. There is, however, a reflected harmonic wave with the electric vector in the plane of reflection. The reflected-harmonic amplitude has been expressed in terms of the nonlinear volume polarization by Bloembergen and Pershan.[18] Equation (4.12) or (4.13) of their paper with $\alpha=0$ gives,

$$E_{R,\mathrm{vol}}(2\omega)=\frac{4\pi P^{\mathrm{NLS}}\epsilon^{-1/2}(\omega)\sin\theta_i}{\epsilon^{1/2}(2\omega)\{1-\epsilon^{-1}(2\omega)\sin^2\theta_i\}^{1/2}+\epsilon(2\omega)\cos\theta_i}. \quad (9)$$

Here θ_i is the angle of incidence of the fundamental wave on the plane plasma boundary, $\epsilon(\omega)$ is the transverse linear dielectric constant of the plasma. P^{NLS} is given by Eq. (8) and it should be remembered that E_0 in that expression is the electric field after refraction just inside the plasma. This E_0 should be computed from the incident amplitude with the appropriate linear Fresnel equation. For a metallic reflector this implies a considerable reduction in its numerical value. A quantitative discussion will be postponed until the next section. There it will be shown that there are surface terms which may contribute more than the volume polarization. This is perhaps not too surprising, since the volume term is essentially a magnetic dipole term which vanishes, for constant ω, in the limit $q\to 0$.

When the incident electric vector is normal to the plane of incidence, there is, however, no surface contribution. In this case the reflected amplitude $E_R(2\omega)$ from Eqs. (8) and (9) and Fresnel's equation may be expressed in terms of the incident amplitude $E^{(i)}$ as follows:

$$E_R(2\omega)=\frac{-4\pi iNe^3}{4m^2c\omega^3(1-\frac{1}{4}x^2)}\times\frac{\sin\theta_i}{[(\cos^2\theta_i-\frac{1}{4}x^2)^{1/2}+(1-\frac{1}{4}x^2)\cos\theta_i]}\times\frac{4\cos^2\theta_i}{[\cos\theta_i+(\cos^2\theta_i-x^2)^{1/2}]^2}(E_\perp^{(i)})^2. \quad (10)$$

Here $x=\omega_p/\omega$, and $\omega_p^2=4\pi Ne^2/m$ is the plasma frequency. The dielectric constants have been taken in the limit $q\to 0$,

$$\epsilon(\omega)=1-\omega_p^2/\omega^2,$$
$$\epsilon(2\omega)=\epsilon_{\mathrm{SCF}}(2\omega,0)=1-\omega_p^2/4\omega^2.$$

Except for the factor $\epsilon_{\mathrm{SCF}}^{-1}$, noted above, this result agrees with a calculation by Jha[19] on the basis of the Boltzmann transport equation for a free-electron gas.

III. THE SECOND-HARMONIC SURFACE POLARIZATION

Jha called attention to the importance of surface terms which are connected with the discontinuity of the normal component of the electric field at the boundary. For these terms it is essential that the incident field has a component in the plane of incidence. Choose a coordinate system where this plane is the xz plane and let $\hat{z}$ be the direction normal to the boundary. According to the macroscopic equations the discontinuity in the normal component is described by

$$\partial E_z/\partial z=[1-\epsilon^{-1}(\omega)]E_{z=+0}\delta(z),$$

[17] See Ref. 3, or N. Bloembergen, *Nonlinear Optics* (W. A. Benjamin and Company, New York, 1965).

[18] N. Bloembergen and P. S. Pershan, Phys. Rev. **128**, 606 (1962). There is a misprint in Eq. (4.12) of this paper. The denominator of the last term should read "$\epsilon_T^{1/2}\epsilon_R^{1/2}\cos\theta_T+\epsilon_T\cos\theta_R$" instead of "$\epsilon_T^{1/2}\epsilon_S^{1/2}\cos\theta_T+\epsilon_T\cos\theta_R$."

[19] See Ref. 4. The authors are indebted to Dr. Jha for a helpful discussion.

where $E_{z=+0}$ is the normal component of the transmitted wave just outside the plasma. It consists of the sum of the normal components of the incident and reflected waves and is $\epsilon(\omega)$ times larger than the normal component just inside the plasma.

In a microscopic picture there is of course no strict discontinuity. The normal component E_z varies rapidly over about one Thomas-Fermi screening length in the case of a metal. In the case of semiconductors, insulators or any other medium one can still expect that the field component changes rapidly over about one interatomic distance. For a detailed calculation a precise knowledge of the surface potential and the surface-state wave function would be required.

Fortunately, the radiation field of a thin slab of polarization, $0 < z \ll \lambda$, does not depend sensitively on the distribution of the polarization as a function of z, but only on the integral $\int P dz$. The second-harmonic surface polarization may therefore be calculated in the following manner: The discontinuity in the normal component of the fundamental frequency induces a free charge density at the surface

$$\rho(\mathbf{r},\omega) = (1/4\pi e)[1-\epsilon^{-1}(\omega)]E_{z=+0}\delta(z)e^{ik_x x - i\omega t}. \quad (11)$$

For a free-electron gas the current density induced by a field $A(\mathbf{r},\omega)$ for an electron density $\rho^{(0)}(\mathbf{r}) = N$ is

$$\langle \mathbf{j}(\omega)\rangle = \mathbf{j}^{(1)}(r,\omega)\rho^{(0)} = (Ne^2/mc)\mathbf{A}(\mathbf{r},\omega) = (Ne^2/im\omega)\mathbf{E}(\mathbf{r},\omega).$$

In the same manner the second-harmonic current density corresponding to the oscillating free charge density (11) at the surface is

$$\langle \mathbf{j}^{(\mathrm{surf})}(2\omega)\rangle = (e/4\pi im\omega)[1-\epsilon^{-1}(\omega)] \times \mathbf{E}(\omega)E_{z=+0}(\omega)\exp(2ik_x x). \quad (12)$$

For the normal component of this surface current density there is some ambiguity in Eq. (12) whether one should take the normal component of $\mathbf{E}(\omega)$ just outside or inside the plasma. If one takes half the sum of these values, the normal surface current density becomes

$$j_z^{(\mathrm{surf})}(\mathbf{r},2\omega) = (e/4\pi im\omega)[1-\epsilon^{-1}(\omega)] \times [\tfrac{1}{2}+\tfrac{1}{2}\epsilon^{-1}(\omega)][E_{z=+0}(\omega)]^2\exp(2ik_x x). \quad (13)$$

It should be noted that this normal component will make the dominant contribution to the reflected harmonic intensity from highly reflecting materials. It follows from the Fresnel equations that the tangential components of the incident and reflected waves at ω nearly cancel each other, while the normal component just outside the surface is almost twice the normal component of the incident field. The normal component $E_{z=+0}$ is expressed in terms of the incident electric field amplitude $E^{(i)}$ which makes an angle φ with the plane of incidence and the direction of the incident beam makes an angle of incidence θ_i with the normal,

$$E_{z=+0}(\omega) = \frac{2\cos\theta_i \sin\theta_i}{\cos\theta_i + \epsilon^{-1/2}(\omega)(1-\epsilon^{-1}(\omega)\sin^2\theta_i)^{1/2}} E^{(i)}\cos\varphi. \quad (14)$$

From Eqs. (13) and (14) it follows that the second-harmonic intensity generated by this surface term is proportional to $\cos^4\varphi$. This dependence has recently been observed by Brown and co-workers[20] for second-harmonic generation from metallic silver. It is therefore of interest to compare the intensity produced by the surface term with the volume terms of the preceding section. The radiation from a thin slab-source distribution has been given by Bloembergen and Pershan.[21] Their Eq. (6.22) may be used with the following substitutions, $-2i\omega P^{\mathrm{NLS}}d = j_z^{\mathrm{surf}}$, $\alpha = \pi - \theta_s$, $\epsilon_T = \epsilon(2\omega)$, $\epsilon_M^{-1/2}\sin\theta_M = \sin\theta_i$, $\epsilon_M = \epsilon(\omega)$. The result is

$$E_R^{\mathrm{surf}}(2\omega) = \frac{2\pi\epsilon^{-1}(\omega)\sin\theta_i c^{-1}}{\cos\theta_i + \epsilon^{-1/2}(2\omega)(1-\epsilon^{-1}(2\omega)\sin\theta_i)^{1/2}} \times j_z^{\mathrm{surf}}(2\omega). \quad (15)$$

When θ_i approaches zero, this field rapidly becomes very small, because $j_z(2\omega)$ itself approaches zero, as well as the factor $\sin\theta_i$. In that case the tangential components of the surface source in Eq. (12) should be taken into account. The radiation field can quite generally be calculated with Eqs. (6.12) and (6.22) of Ref. 18. The resulting harmonic amplitudes should be added to those obtained from the volume polarization and subsequently squared to obtain the second-harmonic intensity. The resulting equations for arbitrary polarization direction φ and arbitrary angle of incidence θ_i of the fundamental field are cumbersome and will not be reproduced here. The detailed results are essentially the same as those of Jha.[21]

It is, however, of interest to compare the order of magnitude of the volume term given by Eqs. (8) and (9) with the surface term given by Eqs. (12), (14), and (15) near angles $\theta_i = \varphi = \pi/4$, where the angular factors do not have zero's. Leaving out all angular factors, the ratio of the second-harmonic amplitudes resulting from the surface contribution given by Eq. (15) and the volume contribution given by Eq. (10) has the order of magnitude $(\omega^2/\omega_p^2)\epsilon(\omega)$, or about unity for $\omega < \omega_p$. On the basis of these calculations, it is doubtful that the observed SHG from metallic silver by Brown *et al.* has its origin in a plasma effect. When the experimental value[22] $\omega_p/\omega = 2.2$, instead of 5, is used in Jha's equations, an observable volume effect should remain, when

[20] F. Brown, R. E. Parks, and A. M. Sleeper, Phys. Rev. Letters **14**, 1029 (1965).

[21] S. S. Jha, Phys. Rev. Letters **15**, 412 (1965). This paper appeared after our manuscript had been submitted. The experimental points should be compared with a theoretical calculation for $\omega_p/\omega = 2.2$ rather than 5.

[22] H. Ehrenreich and H. R. Phillip, Phys. Rev. **128**, 1622 (1962).

the incident field is polarized normal to the plane of incidence.

It has been suggested that the silver ion cores[23] of the surface layer play a dominant role in the SHG. Further support that one does not deal with a plasma effect comes from the observation by Bloembergen and Chang[23] that silicon, germanium and other insulating material with bulk inversion symmetry also show a reflected second-harmonic intensity with a $\cos^4\varphi$ dependence on the angle between the incident electric field and the plane of incidence. The atoms in the surface layer are not at positions of inversion symmetry, and if the incident electric field has a component normal to the surface, large harmonic dipole moments can be induced in these atoms.

The dominant term for these bound electrons in the interaction Hamiltonian is the term

$$\mathcal{H}^{(1)} = -(e/2mc)(\mathbf{p}\cdot\mathbf{A}+\mathbf{p}\cdot\mathbf{A}) \approx -(e\hbar/2imc)(\partial A_z/\partial z+2\mathbf{A}\cdot\nabla).$$

It should be kept in mind that A_z varies rapidly in the first atomic layer and that $\partial A_z/\partial z$ there is so large that the "quadrupole-like" contribution from this term has the same order of magnitude as an electric dipole contribution. The detailed matrix elements of $\mathcal{H}^{(1)}$, which is very inhomogeneous over the surface orbital function ψ_s, are difficult to evaluate. Because both $\mathcal{H}^{(1)}$ and ψ_s have even and odd terms in z, the following nonlinear current density is induced in the surface atoms,

$$\mathbf{j}_{\text{bound}}(2\omega,\mathbf{r}) = N_0 \sum_{n,n'} \frac{\langle\psi_s(\mathbf{r}_0)|\mathbf{j}^{(0)}(\mathbf{r})|n(\mathbf{r}_0)\rangle\langle n|\mathcal{H}^{(1)}|n'\rangle\langle n'|\mathcal{H}^{(1)}|\psi_s\rangle}{(W_s-W_n+\hbar\omega)(W_s-W_{n'}+2\hbar\omega)}$$

+other terms which differ in the order of the operators and in the frequency denominators. (16)

The number of atoms per unit volume is N_0. The current density operator is defined by

$$\mathbf{j}^{(0)}(\mathbf{r}) = \delta(\mathbf{r}-\mathbf{r}_0)\cdot(\hbar e/2im)\nabla+(\hbar e/2im)\nabla\delta(\mathbf{r}-\mathbf{r}_0). \quad (17)$$

For media with inversion symmetry, the second harmonic source density given by Eq. (16) is appreciable only in a surface layer of thickness d, where d is about one interatomic distance, or the Thomas-Fermi screening distance in a metal.

A rough estimate of the bound surface states can be obtained as follows. It is known that the core polarizability of silver ions contributes appreciably to the dielectric constant of the metal in the near ultraviolet.[24] It is therefore not unreasonable to assume the same nonlinear polarizability for a silver ion at the surface as for a GaSb or InAs molecule in the bulk of those piezoelectric crystals. The current density integrated over a layer of thickness d gives therefore a surface source $2i\omega\chi^{\text{NL}}dE_{z=+0}^2$, where $\chi^{\text{NL}}\sim10^{-6}$ esu as for GaSb, and $d\sim2\times10^{-8}$ cm. This should be compared with the plasma-surface source of magnitude $(e/4\pi m\omega)\times E_{z=+0}^2$ according to Eq. (13). One finds for the ratio of bound-surface to plasma-surface contribution $8\pi m\omega^2\times\chi^{\text{NL}}de^{-1}\approx8$ in our numerical example. For the second-harmonic intensity this ratio must be squared, and the bound electron in the surface layer could easily contribute one or two orders of magnitude more than the total plasma contribution. For the bound-surface electrons the same symmetry considerations hold as for the plasma effect. The surface layer is amorphous and essentially isotropic for directions in the plane of the boundary. The current density has tengential component j_x proportional to E_xE_z and j_y proportional to E_yE_z. The normal component j_z proportional to E_z^2 will be dominant for good reflectors since the normal component E_z is much larger than the tangential components in that case. The second-harmonic intensity is consequently proportional to j_z^2 or $\cos^4\varphi$, and the electric field $E_R(2\omega)$ should lie in the plane of reflection. The effect should occur quite generally at the surface of dense polarizable media, including liquids. The SHG should not depend strongly on the plasma density. The available observations on silver, silicon, and germanium are in agreement with this picture.

IV. THE RAMAN SUSCEPTIBILITY OF A PLASMA

The next higher order nonlinearities may be calculated in a similar manner. In principle, again volume and surface terms should be considered. The most important case is the volume effect, which occurs when two electromagnetic waves traverse the plasma, with a difference in frequency close to the plasma frequency. The vector potential in Eq. (2) now consists of four terms with amplitudes A_L, A_L^*, A_s, and A_s^* and frequencies ω_L, $-\omega_L$, ω_s, and $-\omega_s$, respectively. The dominant term in the density-matrix quadratic in the field amplitudes results from the resonance which occurs when $\omega_L-\omega_s$ is near the plasma frequency. In analogy with Eq. (5) one finds immediately,

$$\langle\mathbf{k}|\rho^{(\omega_s-\omega_L)}|\mathbf{k}+\mathbf{q}_s-\mathbf{q}_L\rangle = \frac{f_0(\epsilon_{\mathbf{k}+\mathbf{q}_s-\mathbf{q}_L})-f_0(\epsilon_{\mathbf{k}})}{\epsilon_{\mathbf{k}+\mathbf{q}_s-\mathbf{q}_L}-\epsilon_{\mathbf{k}}+\hbar(\omega_s+\omega_L)+i\Gamma}\frac{2e^2A_sA_L^*}{2mc^2}\times\epsilon_{\text{SCF}}(\omega_L-\omega_s,\,\mathbf{q}_L-\mathbf{q}_s).$$

For $\omega_L-\omega_s\sim\omega_p$, $\text{Re}\,\epsilon_{\text{SCF}}\approx0$, a resonance occurs. Large density fluctuations are induced at the difference frequency, which beat again with the incident laser field at ω_L. In this manner a current density at the Stokes frequency ω_s is induced, which is cubic in the field

[23] See paper by N. Bloembergen and R. K. Chang in Ref. 11.
[24] See Ref. 22.

amplitudes,

$$\mathbf{j}_{\text{Raman}}(\omega_s,\mathbf{q}_s)=\sum_{\mathbf{k}}\langle\mathbf{k}|\rho^{+(\omega_s-\omega_L)}|\mathbf{k}+\mathbf{q}_s-\mathbf{q}_L\rangle\langle\mathbf{k}+\mathbf{q}_s-\mathbf{q}_L|-(e^2/mc)A_L|\mathbf{k}+\mathbf{q}_s\rangle$$

$$=\frac{-e^4|A_L|^2A_s}{m^2c^3\epsilon_{\text{SCF}}^*(\omega_L-\omega_s,\,\mathbf{q}_L-\mathbf{q}_s)}\times\sum_{\mathbf{k}}\frac{f_0(\epsilon_{\mathbf{k}+\mathbf{q}_s-\mathbf{q}_L})-f_0(\epsilon_k)}{\epsilon_{\mathbf{k}+\mathbf{q}_s-\mathbf{q}_L}-\epsilon_{\mathbf{k}}+\hbar(\omega_s-\omega_L)-i\hbar\Gamma}. \quad (18)$$

When the plasmon energy is considered to be the leading term in the denominator, $\hbar(\omega_L-\omega_s)\gg(\hbar^2/2m)\times(\mathbf{q}_L-\mathbf{q}_s)\cdot\mathbf{k}_F$ and $\omega_L-\omega_s>\Gamma$, an expansion of the denominator yields for Eq. (18) the simple expression,

$$\mathbf{j}_{\text{Raman}}(\omega_s,\mathbf{q}_s)=\frac{-Ne^4|A_L|^2\mathbf{A}_s}{m^3c^3\epsilon_{\text{SCF}}^*(\omega_L-\omega_s,\,\mathbf{q}_L-\mathbf{q}_s)}\frac{(\mathbf{q}_L-\mathbf{q}_s)^2}{(\omega_L-\omega_s)^2}. \quad (19)$$

For forward Raman scattering the last factor may be replaced by c^{-2}. It should be noted that the picture of resonance with a plasma wave only has validity for $|\mathbf{q}_L-\mathbf{q}_s|\ll L_D^{-1}$ where L_D is the Debye length of the plasma. For larger values the real part of $\epsilon_{\text{SCF}}(\omega,\,\mathbf{q}_L-\mathbf{q}_s)$ cannot be made equal to zero. For gaseous plasmas, the resonance occurs only near the forward direction. At the plasma resonance ϵ_{SCF}^* is negative imaginary and has a value $-i(\omega_p\tau)^{-1}$, where the decay time for the power is determined by the Landau damping rate and the collision rate $\tau^{-1}=\tau_{\text{Landau}}^{-1}+\tau_{\text{coll}}^{-1}$. One may again replace the current density by an equivalent polarization and the vector potentials by the corresponding electric field amplitudes. In this manner the Raman susceptibility for a plasma is introduced. For resonant scattering in the forward direction one finds

$$\mathbf{P}(\omega_s,\mathbf{q}_s)=\chi_{\text{Raman}}|E_L|^2\mathbf{E}_s=\frac{-iNe^4}{\omega_s^2\omega_L^2m^3c^2(\omega_p\tau)}|E_L|^2\mathbf{E}_s. \quad (20)$$

Off resonance, where $\epsilon_{\text{SCF}}\sim1$, one should replace $i\omega_p\tau$ by unity in Eq. (20). In that case the same formula could have been obtained from a very elementary independent electron model.

The Raman polarization given by Eq. (20) is 90° out of phase with the Stokes field $\mathbf{E}_s$. The susceptibility is negative imaginary and produces an exponential gain at the frequency ω_s. If one takes a plasma characterized by the same parameters as the case considered by Kroll, Ron, and Rostoker,[25] $n_0=10^{14}$ cm^{-3}, $\omega_p\tau=10^3$, and $\omega_L=\omega_s+\omega_p=2\pi(4\times10^{14})^{-1}$, one finds $\chi_{\text{Raman}}^{\text{plasma}}\approx10^{-22}$ esu. This is about ten orders of magnitude smaller than the Raman susceptibility of liquids ordinarily used in Raman lasers. Since the plasma frequency is very small compared to the light frequency in this example, the susceptibility can be considerably enhanced by introducing a small angle between the Stokes and the laser beam. In that case one should return to the more general expression Eq. (19). The optimum value of

$$[\epsilon_{\text{SCF}}''(\omega_L-\omega_s,\,\mathbf{q}_L-\mathbf{q}_s)]^{-1}(\mathbf{q}_L-\mathbf{q}_s)^2(\omega_L-\omega_s)^{-2}$$

can be made about a factor 10^4 larger in this example than $(\omega_p\tau)c^{-2}$ which it assumes in the forward direction. The nonlinear susceptibility for this optimum direction, occurring at angle of about 10^{-2} radian between the two light beams, is still six orders of magnitude smaller than that in ordinary Raman liquids. It is doubtful that the stimulated Raman effect in a plasma will lead to observable effects.

Since Kroll and co-workers arrived at a more optimistic conclusion, it is of interest to show that our result can be reconciled numerically with their equation for a scattering cross section per unit solid angle. They, and other workers, considered a scattering process involving four light quanta with frequencies ω_1, ω_2, ω_3, and ω_4, satisfying the energy and momentum conservation relationships $\omega_4-\omega_3=\omega_2-\omega_1=\omega_p$, and $\mathbf{q}_4-\mathbf{q}_3=\mathbf{q}_2-\mathbf{q}_1$. Although the calculation for this cross section is considerably more complicated in scattering theory than the calculation of an inelastic Raman scattering involving only the two quanta ω_L and ω_s, the calculation of the corresponding complex nonlinear susceptibility is straightforward and essentially the same as for the Raman process. The complex susceptibilities automatically take account of all questions of phase coherence and elastic and inelastic scattering processes. In direct analogy to Eq. (20), one finds a polarization at ω_4,

$$P^{\text{NL}}(\omega_4=\omega_2+\omega_3-\omega_1)=\frac{-n_0e^4(\mathbf{q}_2-\mathbf{q}_1)^2}{\omega_1\omega_2\omega_3\omega_4m^3(\omega_2-\omega_1)^2\epsilon_{\text{SCF}}^*(\omega_2-\omega_1,\,\mathbf{q}_2-\mathbf{q}_1)}E_2E_3E_1^*. \quad (21)$$

For $\omega_2=\omega_3=\omega_L$, ω_4 represents, of course, the anti-Stokes frequency.

Consider a homogeneous interaction region in the plasma of volume $V=Al$, where A is the cross-sectional area of the three beams E_1, E_2, and E_3 and l is the length. The field strength E_4 of the phase-matched wave at ω_4, which is parametrically generated in the volume V, is given by[26]

$$E_4=4\pi P^{\text{NL}}(\omega_4=\omega_2+\omega_3-\omega_1)\omega_4c^{-1}l. \quad (23)$$

The total power radiated at ω_4 is

$$I_4=\frac{c}{2\pi}A|E_4|^2=\frac{8\pi n_0^2e^8|E_1|^2|E_2|^3|E_3|^2}{m^6c^5\omega_1^2\omega_2^2\omega_3^2|\epsilon_{\text{SCF}}|^2}Al^2. \quad (23)$$

[25] See Ref. 8.

[26] See Ref. 17.

A factor 2π rather than 8π is used in the denominator of the Poynting vector because our amplitudes are defined in Eq. (2) as twice the conventional ones. In this form the result may be compared with the scattering cross section per electron for a four-photon collision, $\omega_3+\omega_2 \rightarrow \omega_1+\omega_4$, given by Kroll, Ron, and Rostoker,

$$\frac{d\sigma}{d\Omega}=\frac{(e^2/mc^2)^2k^4|E_1|^2|E_2|^2}{32(2\pi)^3m^2n_0\omega_1{}^2\omega_2{}^2|\epsilon_{\mathrm{SCF}}|^2}\delta(\mathbf{k}-\Delta\mathbf{k}), \quad (24)$$

where $k^2=\omega_p{}^2/c^2=4\pi n_0e^2/mc^2$ and $\delta(\mathbf{k}-\Delta\mathbf{k})\approx V$, and the amplitudes now have the conventional definition. The total cross section for the volume V, integrated over the solid angle $d\Omega$, which is determined by the diffraction limit from an area A, $d\Omega=(4\pi^2c^2/\omega_3\omega_4)A^{-1}$, is obtained by multiplying Eq. (24) by $n_0Ald\Omega$,

$$\sigma_{\mathrm{total}}=\frac{\pi n_0{}^2e^8Al^2|E_1|^2|E_2|^2}{m^6c^6\omega_1{}^2\omega_2{}^2\omega_4\omega_3|\epsilon_{\mathrm{SCF}}|^2}. \quad (25)$$

The number of incident quanta in the beam at ω_3 per second is $c|E_3|^2A/8\pi\hbar\omega_3$. The number of scattered quanta at ω_4 is

$$c|E_3|^2\sigma_{\mathrm{total}}/8\pi\hbar\omega_3$$

and the total scattered intensity at ω_4 is

$$I_4=(\omega_4/\omega_3)c|E_3|^2\sigma_{\mathrm{total}}/8\pi. \quad (26)$$

When Eq. (25) is substituted into Eq. (26), a result is obtained that is a factor 2^6 smaller than given by Eq. (23). This difference may be ascribed to the difference in definition of the field amplitudes. The amplitudes defined by Eq. (2) and used in Eq. (23) are a factor 2 smaller than the conventional amplitudes used in Eqs. (24–26).

Although there is formal agreement between the two results, the rather more optimistic estimate of detectability by Kroll and co-workers can be traced to their use of the scattering cross section per unit solid angle. For a diffraction limited beam the total available solid angle is quite small, and the total scattered intensity is probably more significant from an experimental point of view. Baym and Hellwarth have independently arrived at a similar conclusion.[27]

In a metal plasma the electron density can be higher by eight orders of magnitude than in the preceding example, while the quality factor $\omega_p\tau$ of the plasma resonance in silver can be taken as 10^2. The nonlinear susceptibiliby for two ultraviolet beams could thus be substantially higher than a gaseous plasma. Unfortunately the transparency of metals for frequencies $\omega>\omega_p$ is far from perfect due to excitation of core electrons. The absorption from powerful ultraviolet beams, if these were available, would probably be prohibitive. The best possibility to detect the stimulated Raman effect in a plasma would appear to be for infrared beams in a semiconductor plasma. Spontaneous inelastic or Raman scattering should be easier to detect than the stimulated effects.

[27] Paper by G. Baym and R. W. Hellwarth in Ref. 11.

V. THE INTERACTION BETWEEN TWO LIGHT WAVES AND A PLASMA WAVE

The Raman and Brillouin effect in liquids and solids can be described as the parametric interaction between two light waves and a vibrational wave. When the optical or acoustical phonon wave is heavily damped, this description is equivalent to one in terms of Raman susceptibilities.[28] In this section the Raman effect in a plasma will be described in terms of a parametric interaction between two light waves and a plasma wave. An equivalent discussion with detailed numerical examples has independently been given by Cosimar.[29]

Consider a small volume element at the point $\mathbf{r}$. Let the average deviation of the electrons from their equilibrium position in this volume element be $\mathbf{u}(\mathbf{r})$. Introduce normal coordinates $Q_{\mathbf{k}}$ as the Fourier transform of this average deviation or local strain of the electron gas,

$$\mathbf{Q}_k=\int\mathbf{u}(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}d^3r.$$

The canonical conjugate to this variable is $\mathbf{P}_{\mathbf{k}}$. The Hamiltonian density for the plasma waves then takes the form,[30]

$$\mathcal{H}_{\mathrm{plasma}}=\tfrac{1}{2}\sum_{\mathbf{k}}\big((1/Nm)\mathbf{P}_{\mathbf{k}}\cdot\mathbf{P}_{-\mathbf{k}}+\alpha k^2\mathbf{Q}_{\mathbf{k}}\cdot\mathbf{Q}_{-\mathbf{k}}+4\pi N^2e^2\mathbf{Q}_{\mathbf{k}}\cdot\mathbf{Q}_{-\mathbf{k}}\big). \quad (27)$$

Here N is the average number of electrons per unit volume and α is the bulk modulus of the electron gas. The fluctuation in the electron density from the average due to the presence of plasma waves is

$$\delta\rho(\mathbf{r})=N\,\mathrm{div}\mathbf{u}=iN\sum_{\mathbf{k}}\mathbf{k}\cdot\mathbf{Q}_ke^{i\mathbf{k}\cdot\mathbf{r}}.$$

The change in the interaction of the two light waves with the electrons in a unit volume due to the presence of the plasma waves is consequently

$$\mathcal{H}_{\mathrm{int}}=(e^2/2mc^2)\mathbf{A}^2\delta\rho(\mathbf{r}),$$

where

$$\mathbf{A}=\mathbf{A}_Le^{i\mathbf{q}_L\cdot\mathbf{r}-i\omega_Lt}+\mathbf{A}_se^{i\mathbf{q}_s\cdot\mathbf{r}-i\omega_st}+\text{c.c.}$$

When all nonresonant perturbations are truncated, the interaction Hamiltonian density between the two linear parallel polarized light waves and the longitudinal plasma waves $(\mathbf{Q}\|\mathbf{k})$ becomes,

$$\mathcal{H}_{\mathrm{int}}=(iNe^2/mc^2)\sum_{\mathbf{k}}kA_LA_s{}^*Q_k{}^*e^{i(\mathbf{q}_L-\mathbf{q}_s-\mathbf{k})\cdot\mathbf{r}}+\text{c.c.} \quad (28)$$

[28] See Ref. 15.

[29] G. C. Cosimar (private communication). The authors are indebted to Dr. Cosimar for receiving a copy of a forthcoming paper.

[30] See, for example, C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963) p. 35.

The equations of motion for the plasma coordinate are

$$\dot{P}_k = -\partial(\mathcal{H}_{\text{plasma}}+\mathcal{H}_{\text{int}})/\partial Q_k,$$
$$\dot{Q}_k = +\partial(\mathcal{H}_{\text{plasma}}+\mathcal{H}_{\text{int}})/\partial P_k.$$

These equations of motion can be combined into a wave equation for Q_k. Because of the presence of $\mathcal{H}_{\text{int}}$ a driving term proportional to the light amplitudes $A_L A_s^*$ is added to the plasma wave equation. Landau damping and damping by collisions may be taken into account by a phenomenological damping term,

$$\ddot{Q}_k+\alpha\nabla^2 Q_k+\omega_p^2 Q_k = (ie^2k/m^2c^2)A_L A_s^* + (2i\omega_k/\tau')Q_k. \quad (29)$$

The exponential factor

$$\exp\{i(\mathbf{q}_L-\mathbf{q}_s-\mathbf{k})\cdot\mathbf{r}-i(\omega_L-\omega_s-\omega_k)t\}$$

can be dropped from the inhomogeneous driving term, because the effect of coupling between the light waves and plasma wave will be small unless the conditions of conservation of energy and momentum are satisfied, $\omega_L-\omega_s=\omega_k$ and $\mathbf{q}_L-\mathbf{q}_s=\mathbf{k}$. The plasma wave concept only has validity, if its wavelength is long compared to the characteristic Debye length. For the most important case of forward scattering with parallel laser and stokes beams this condition will usually be satisfied. One may then write $k=q_L-q_s=\omega_p/c$, because the dispersion in the plasma frequency will then be negligible since $(\alpha/Nm)(q_L-q_s)^2\ll\omega_p^2$. The characteristic time τ' in Eq. (29) refers to the decay time for the amplitude. The decay rate for the power is related to the imaginary part of the longitudinal dielectric constant by $2\tau'^{-1}=\epsilon_{\text{SCF}}''\omega_p$.

The wave equations for the light amplitudes A_L and A_s are also augmented by a nonlinear term, because the interaction Hamiltonian gives rise to a nonlinear current density,

$$j^{\text{NL}}(\omega_s) = -c\partial\mathcal{H}_{\text{int}}/\partial A_L^* = (+iNe^2/mc)kA_L Q_k^* \quad (30)$$

and a similar expression for $j^{\text{NL}}(\omega_L)$. The wave equations for the two light waves become, consequently,

$$-\ddot{A}_L+c^2\nabla^2 = (4\pi iNe^2/m)kA_s Q_k, \quad (31)$$
$$-\ddot{A}_s+c^2\nabla^2 = (4\pi iNe^2/m)kA_L Q_k^*. \quad (32)$$

The set of three coupled nonlinear wave equations is familiar from the Brillouin and Raman effect in other media. If the laser amplitude can be taken as a constant parameter, a set of two linear coupled equations (29) and (32) for A_s and Q results. An exact solution can readily be written down, but the following approximate solution will be adequate for our purposes. Since the plasma wave is heavily damped its amplitude is essentially the driven steady state value, when the right-hand side of Eq. (29) is separately put equal to zero. When the value of Q so obtained is substituted back into Eq. (30), one obtains for forward scattering,

$$j^{\text{NL}}(\omega_s) = \frac{Ne^4k^2}{m^3c^3\omega_p^2\epsilon_{\text{SCF}}''}|A_L|^2A_s = \frac{Ne^4}{m^3c^5\epsilon_{\text{SCF}}''}|A_L|^2A_s. \quad (33)$$

This is identical to the result of Eq. (19) taken at resonance, $\epsilon_{\text{SCF}}'=0$. The equivalence of the two different ways to describe the interaction between photons and plasmons is thus established. When the value of Q is substituted into the wave equation (32), one obtains the exponential gain at the Stokes frequency. Coupling with anti-Stokes waves in the plasma, etc., can of course be treated in the same manner.

VI. CONCLUSION

The optical nonlinearities of a plasma can be treated by the same methods that have been used to describe the nonlinear optical properties of other media. The nonlinearities of the plasmas are generally smaller by many orders of magnitude, because they would vanish altogether for free electrons in the electric dipole approximation.

Although spontaneous nonlinear scattering processes in certain plasmas may be detectable, stimulated Raman effects would hardly be accessible to experimental observation at optical frequencies. The situation is of course much more favorable in the far infrared and microwave region. Even the lower order nonlinear process of second-harmonic generation from a plasma has not been established experimentally at optical frequencies. The second-harmonic radiation observed from a silver surface is shown to have its origin in the nonlinearity of bound electrons in the ion cores of a monatomic surface layer.