two phonons having wave vectors in the neighborhood of points like (0.4,0.4,0.4) and frequencies near 2.6. The conditions $\omega=\omega_1+\omega_2$ and $\mathbf{Q}=\mathbf{Q}_1+\mathbf{Q}_2$ can be fulfilled simultaneously in this neighborhood (ω, $\mathbf{Q}$ refer to the primary phonon, ω_1, $\mathbf{Q}_1$, ω_2, $\mathbf{Q}_2$ to the secondary phonons) if we take $\mathbf{Q}_1$ near (0.4,0.4,0.4) and $\mathbf{Q}_2$ near (0.4, −0.4, −0.4) for case 1 and $\mathbf{Q}_1$ near (0.4, 0.4, 0.4), $\mathbf{Q}_2$ near (−0.4, 0.4, 0.4) for case 3. The secondary phonons here are near the flat maximum of the [1,1,1]T curve, and we may expect a high density of states on the final side of the transition. Unfortunately, proper confirmation of this suggested singularity calls for a major effort of computation which is beyond our scope; the argument put forward here is merely one of plausibility.

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Second-Order Optical Processes and Harmonic Fields in Solids

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A consistent method has been developed to calculate induced electromagnetic fields and optical transitions of electrons in a solid, in response to an incident laser beam of (circular) frequency ω. The analysis is based upon the independent-particle Schrödinger equation for electrons and Maxwell's equations for the electromagnetic fields. General expressions for linear and bilinear currents as well as second-order optical transition probabilities have been derived. It is shown that the second-order transition probability, which is proportional to the fourth power in the incident field, contains two different types of terms, describing double-photon transitions of the incident frequency ω and single-photon transitions of the harmonic frequency 2ω. An estimate has been made to show that in the case of centrosymmetric solids like metals, the relative contribution due to the single second-harmonic photon transition is of the order $(e^2/\hbar c)^2 \ll 1$ in the optical region, compared with the double-fundamental-photon transition. However, in the case of solids lacking inversion symmetry, the contributions due to these two processes are estimated to be of the same order in magnitude.

1. INTRODUCTION

AFTER the discovery[1] of lasers it has now become possible to observe[2] second-order optical transitions of electrons in solids. Usually one assumes[3] the physical process involved in such cases to be either emission or absorption of two photons of incident (circular) frequency ω. However, the powerful laser beams required for these observations also produce harmonic fields in the solid. An electron in the solid does not move in the incident field of frequency ω but in a self-consistent local field which contains the fundamental field proportional to the incident field, and other harmonic fields of higher order in the incident field. In particular, the second harmonic field is proportional to the square of the incident field. Contributions to the second-order optical transition probability proportional to the fourth power of the incident field may therefore come not only from double-photon transitions of the fundamental field but also from single-photon transitions of the induced second harmonic field. The purpose of this paper is to study the relative importance of these two processes.

Several theoretical calculations[4–9] of nonlinear polarizability, from which induced fields may be deduced by solving[10] Maxwell's equations, have been published. These methods are distinguished by the nature of simplifying assumptions and by the stage at which they are introduced. However, in most of these investigations only electric-dipole transitions have been considered and they have therefore only restricted applications.

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For example, this type of calculation is not useful for centrosymmetric metals where lowest order contributions to nonlinear polarizability do not come from electric-dipole transitions and where the surface effect[11] also is very important. Cheng and Miller[12] developed a theory specially suited for a metal but their assumption of an infinite solid restricts its application in analyzing most of the experimental results. A more complete theory for metals[13] was considered by us in I where we used the classical Boltzmann equation for the electrons. The approach to be followed in this paper is to formulate a general self-consistent quantum-mechanical theory which will not only take into account the second- and higher order optical processes and harmonic generations in a unified way but where final algebraic expressions will be written in simple, concise, and more familiar terms.

Our calculation is based upon a self-consistent set of Maxwell's equations and the Schrödinger equation, respectively, for the electromagnetic fields and the electrons in the solid. We will neglect the motion as well as the polarization of ions and we will consider the electrons to be moving independently in a self-consistent potential $V(\mathbf{x})$ before the light wave is switched on. The mathematical formulation of the problem and a formal solution of the Schrödinger equation are described in the next section of this paper.

In Sec. 3 we explicitly write down the expressions for linear as well as bilinear currents generated in the solid and calculate them in some simple cases. In Sec. 4 we derive the expression for the second-order transition probabilities and compare the orders of magnitude of different terms in it. We find that in metals where conduction electrons may be considered to be free, the single second-harmonic photon transition probability is indeed negligible. However, for crystals which lack center of inversion the nonlinear polarizability is large compared to metals and we find that the single second-harmonic photon transition probability in this case is of the same order as the double fundamental photon transition probability. One should therefore take this into account in any realistic calculation and it is hoped that the formalism developed in this paper will be useful for this purpose.

2. MATHEMATICAL FORMULATION

In the independent-particle model, unperturbed states of the electrons may be described by the solution of the Schrödinger equation

$$\mathcal{H}_0 u_k^{(0)}(\mathbf{x},t) = i\hbar\frac{\partial u_k^{(0)}}{\partial t}(\mathbf{x},t)\,, \tag{2.1}$$

where

$$\mathcal{H}_0 = (-\hbar^2/2m)\nabla^2 + V(\mathbf{x})\,, \tag{2.2}$$

and where $V(\mathbf{x})$ is the self-consistent potential in which the electrons of mass m are moving. Stationary solutions of Eqs. (2.1) and (2.2) are given by

$$u_k^{(0)} = \Psi_k^{(0)}(\mathbf{x})e^{(-i/\hbar)E_k t}\,, \tag{2.3}$$

with

$$\mathcal{H}_0\Psi_k^{(0)} = E_k\Psi_k^{(0)}\,. \tag{2.4}$$

In the special case where $V(\mathbf{x})$ is a periodic potential it is well known that the solutions $\Psi_k^{(0)}$ may be represented by Bloch waves. When $V(\mathbf{x})$ is taken to be an infinite step potential at $x=0$, $\Psi_k^{(0)}$ is a standing sine-wave in x direction and traveling plane waves in y and z directions. We will not consider any explicit forms of $V(\mathbf{x})$ and $\Psi_k^{(0)}$ in this section but we will just note that all the states[14] up to $\mathbf{k}=\mathbf{k}_F$ (where $\hbar\mathbf{k}_F$ is the Fermi momentum) are occupied by the conduction electrons in the case of metals.

At time $t=-\infty$ a light wave of frequency ω is switched on. This incident light wave is represented by a plane wave with the vector potential

$$\mathbf{A}_{\rm inc} = \mathbf{D}_1 e^{i\mathbf{q}_0\cdot\mathbf{x}}e^{-i\omega t} + \text{Complex Conjugate}, \tag{2.5}$$

and the scalar potential

$$\Phi_{\rm inc} = 0\,, \tag{2.6}$$

where

$$\mathbf{D}_1\cdot\mathbf{q}_0 = 0\,. \tag{2.7}$$

After a sufficiently long time self-consistent electromagnetic fields $\mathbf{E}$ and $\mathbf{H}$ will be set up inside and outside the solid. These fields may be represented by a vector potential $\mathbf{A}$ and a time-independent scalar potential Φ_0. We have thus chosen a gauge where the time-dependent part of the scalar potential is zero. The single-particle Schrödinger equation now becomes

$$(\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_2)u_k = -i\hbar(\partial u_k/\partial t)\,, \tag{2.8}$$

where

$$\mathcal{H}_1 = (-i\hbar e/mc)(\mathbf{A}\cdot\nabla+\tfrac{1}{2}\nabla\cdot\mathbf{A}) - e\Phi_0\,, \tag{2.9}$$

and

$$\mathcal{H}_2 = \frac{e^2}{2mc^2}\mathbf{A}\cdot\mathbf{A}\,. \tag{2.10}$$

To be self-consistent $\mathbf{A}$ and Φ_0 must satisfy Maxwell's equations

$$\nabla\times\nabla\times\mathbf{A} + (1/c^2)(\partial^2\mathbf{A}/\partial t^2) = (4\pi/c)\mathbf{J}\,, \tag{2.11}$$

and

$$(-1/c)(\partial/\partial t)(\nabla\cdot\mathbf{A}) - \nabla^2\Phi_0 = 4\pi\rho\,, \tag{2.12}$$

where $\mathbf{J}$ and ρ are current and charge densities, respectively, and where the incoming wave solution of the above equations are given by Eqs. (2.5)–(2.7). In terms of the solutions u_k of Eq. (2.8) the current density is

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[14] In this case our label k specifies the wave vector $\mathbf{k}$ (3 numbers) and the energy band.

given by

$$\mathbf{J}=\frac{-e\hbar}{2mi}\sum_k\left(u_k^*\nabla u_k-u_k\nabla u_k^*\right)-\frac{e^2\mathbf{A}}{mc}\sum_k u_k^*u_k, \qquad (2.13)$$

and the charge density is given by

$$\rho=-e\sum_k\left(u_k^*u_k-n_0\right), \qquad (2.14)$$

where

$$n_0=\sum_k\left(u_k^{*(0)}u_k^{(0)}\right), \qquad (2.15)$$

is the unperturbed density of electrons and en_0 is the charge density of the ions. Summations over k in the above equations go only over occupied states. The current and charge densities satisfy the usual continuity equation

$$(\partial\rho/\partial t)=-\nabla\cdot\mathbf{J}. \qquad (2.16)$$

Now let us assume that

$$\mathbf{A}=\lim_{\epsilon\to 0,\,\epsilon>0}\sum_{l=-\infty}^{l=+\infty}\mathbf{a}_l(\mathbf{x})e^{-il\omega t}e^{\epsilon t/\hbar}, \qquad (2.17)$$

where

$$a_{-l}=a_l^*, \qquad (2.18)$$

and where l assumes all integer values. The factor $e^{\epsilon t/\hbar}$ represents an adiabatic switching of the external field and it is understood that we will put ϵ equal to zero at the end of all our calculations. The expressions for $\mathcal{H}_1$ and $\mathcal{H}_2$ in Eqs. (2.9) and (2.10) then become

$$\mathcal{H}_1=\sum_l \xi_l e^{-il\omega t}e^{\epsilon t/\hbar}, \qquad (2.19)$$

and

$$\mathcal{H}_2=\sum_l \eta_{ll'}e^{-i(l+l')\omega t}e^{2\epsilon t/\hbar}, \qquad (2.20)$$

with

$$\xi_l=(-i\hbar e/mc)(\mathbf{a}_l\cdot\nabla+\tfrac{1}{2}\nabla\cdot\mathbf{a}_l) \quad \text{for} \quad l\neq 0, \qquad (2.21)$$

$$\xi_0=(-i\hbar e/mc)(\mathbf{a}_0\cdot\nabla+\tfrac{1}{2}\nabla\cdot\mathbf{a}_0)-e\Phi_0, \qquad (2.22)$$

and

$$\eta_{ll'}=(e^2/2mc^2)\mathbf{a}_l\cdot\mathbf{a}_{l'}. \qquad (2.23)$$

At time $t=-\infty$ only the $l=\pm 1$ components of the vector potential are switched on and if one treats this as a perturbation on the motion of the electrons it is to be expected that

$$|\mathbf{a}_l|\sim|\mathbf{A}_{\text{inc}}|^{|l|} \quad \text{for} \quad l\neq 0, \qquad (2.24)$$

and the leading terms in $\mathbf{a}_0$ and Φ_0 are of second order in $|\mathbf{A}_{\text{inc}}|$.

To find a formal solution of the time-dependent Schrödinger equation (2.8) we may expand U_k as

$$u_k(t)=\sum_n c_{nk}(t)u_n^{(0)}(t). \qquad (2.25)$$

If one assumes further that the electron under consideration was in the unperturbed state k at time $t=-\infty$, by using Eqs. (2.3), (2.8), (2.19)–(2.23) and the standard time-dependent perturbation technique one obtains

$$c_{nk}=c_{nk}^{(0)}+c_{nk}^{(1)}+c_{nk}^{(2)}+\cdots, \qquad (2.26)$$

where

$$c_{nk}^{(0)}=\delta n,k, \qquad (2.27)$$

$$c_{nk}^{(1)}=\sum_l\langle n|\xi_l|k\rangle\frac{e^{(-i/\hbar)(E_k-E_n+l\hbar\omega)t}e^{\epsilon t/\hbar}}{(E_k-E_n+l\hbar\omega+i\epsilon)}, \qquad (2.28)$$

$$c_{nk}^{(2)}=\sum_l\sum_{l'}\left[\sum_m\frac{\langle n|\xi_l|m\rangle\langle m|\xi_{l'}|k\rangle}{(E_k-E_m+l'\hbar\omega+i\epsilon)}+\langle n|\eta_{ll'}|k\rangle\right]\times\frac{e^{(-i/\hbar)(E_k-E_n+l\hbar\omega+l'\hbar\omega)t}e^{2\epsilon t/\hbar}}{(E_k-E_n+l\hbar\omega+l'\hbar\omega+2i\epsilon)}, \qquad (2.29)$$

and where $\langle n|\xi_l|m\rangle$ and $\langle n|\eta_{ll'}|m\rangle$ are the matrix elements of the operators ξ_l and $\eta_{ll'}$, respectively, between the stationary unperturbed states n and m. In Eq. (2.26), $c_{nk}^{(0)}$ is independent of the induced potentials, $c_{nk}^{(1)}$ is linear, $c_{nk}^{(2)}$ is bilinear and so on. We want to emphasize at this point that the expansion in Eq. (2.26) is not in powers of $|\mathbf{A}_{\text{inc}}|$ and in order to achieve that we will later on rearrange these terms with the help of Eq (2.24).

The perturbed wave function u_k for the electron initially in the state k may now be seen from Eqs. (2.3), and (2.25)–(2.29) to be

$$u_k=\Psi_k^{(0)}(\mathbf{x})e^{-(i/\hbar)E_kt}+\sum_l\Psi_k^{(1)l}(\mathbf{x})e^{-(i/\hbar)(E_k+l\hbar\omega)t}+\sum_{l,l'}\Psi_k^{(2)ll'}e^{-(i/\hbar)(E_k+l\hbar\omega+l'\hbar\omega)t}+\cdots, \qquad (2.30)$$

where

$$\Psi_k^{(1)l}=\sum_n\frac{\langle n|\xi_l|k\rangle\Psi_n^{(0)}}{(E_k+l\hbar\omega-E_n+i\epsilon)}, \qquad (2.31)$$

and

$$\Psi_k^{(2)ll'}=\sum_n\left\{\sum_m\left[\frac{\langle n|\xi_l|m\rangle\langle m|\xi_{l'}|k\rangle}{(E_k+l'\hbar\omega-E_m+i\epsilon)}\right]+\langle n|\eta_{ll'}|k\rangle\right\}\times\frac{\Psi_n^{(0)}}{(E_k+l\hbar\omega+l'\hbar\omega-E_n+2i\epsilon)}. \qquad (2.32)$$

Alternatively, it is equivalent to saying that $\Psi_k^{(1)l}$ and $\Psi_k^{(2)ll'}$ satisfy the differential equations

$$(\mathcal{H}_0-E_k-l\hbar\omega)\Psi_k^{(1)l}=-\xi_l\Psi_k^{(0)}, \qquad (2.33)$$

and

$$(\mathcal{H}_0-E_k-l\hbar\omega-l'\hbar\omega)\Psi_k^{(2)ll'}=-\xi_l\Psi_k^{(1)l'}-\eta_{ll'}\Psi_k^{(0)}, \qquad (2.34)$$

respectively, with an extra restriction that solutions of the homogeneous part of the above equations must be taken as either outgoing or damped waves.

At this point a few words about the superscripts on $\Psi_k^{(s)l_1\cdots l_s}$ are in order. The left-hand superscript in the bracket denotes whether Ψ_k is independent, linear, bilinear, etc. in the induced components of the potential, whereas the superscripts following it denote exactly which components of the potentials occur in the expression for Ψ_k. For example, the superscripts in $\Psi_k{}^{(2)ll'}$ imply that $\Psi_k{}^{(2)ll'}$ is bilinear in $\mathbf{a}_l$ and $\mathbf{a}_{l'}$.

When one expands the current density and the charge density, respectively, as

$$\mathbf{J}(\mathbf{x},t)=\sum_l \mathbf{j}_l(\mathbf{x})e^{-il\omega t}, \tag{2.35}$$

and

$$\rho(\mathbf{x},t)=\sum_l \rho_l(\mathbf{x})e^{-il\omega t}, \tag{2.36}$$

Maxwell's equations, which are to be solved to find the induced potentials, become, for $l\neq 0$,

$$\nabla\times\nabla\times\mathbf{a}_l-[(l^2\omega^2/c^2)\mathbf{a}_l]=(4\pi/c)\mathbf{j}_l, \tag{2.37}$$

$$\nabla\cdot\mathbf{a}_l=(4\pi c/il\omega)\rho_l, \tag{2.38}$$

and for $l=0$,

$$\nabla\times\nabla\times\mathbf{a}_0=(4\pi/c)\mathbf{j}_0, \tag{2.39}$$

$$-\nabla^2\Phi_0=4\pi\rho_0. \tag{2.40}$$

The expressions for components of the charge and current densities on the right-hand sides of these equations may formally be written down by using Eqs. (2.13), (2.14), (2.30), and (2.35). For any l these contain all the components of the unknown potentials, and the above set of equations is thus essentially a set of coupled integrodifferential equations. However, in the perturbation approximation where one keeps only the leading powers of $|\mathbf{A}_{\mathrm{inc}}|$ in $\mathbf{j}_l$, it is possible to uncouple the equations for $l=1$ and in principle to solve for $\mathbf{a}_1$. With this solution for $\mathbf{a}_1$ one may find $\mathbf{j}_2$ which contains only the known $\mathbf{a}_1$ and the unknown $\mathbf{a}_2$, and thus go on to solve the equations for $l=2$. This procedure may be carried forward to any higher l. In the next section we will obtain the expressions for $\mathbf{j}_1$ and $\mathbf{j}_2$ in this approximation. The charge densities may always be written down by using the continuity equation, once the current densities are known.

3. LINEAR AND BILINEAR CURRENTS

In order to calculate the fundamental and second harmonic fields of Eqs. (2.37) and (2.38) we need explicit expressions for the current and charge densities for $l=1$ and $l=2$. By keeping only the lowest order terms in $|\mathbf{A}_{\mathrm{inc}}|$ and by using Eqs. (2.13), (2.14), (2.24), (2.30) and (2.35) one obtains

$$\begin{aligned}\mathbf{j}_1=\frac{-e\hbar}{2mi}\sum_k[&\Psi_k{}^{*(0)}\nabla\Psi_k{}^{(1)1}-\Psi_k{}^{(1)1}\nabla\Psi_k{}^{*(0)}\\&+\Psi_k{}^{*(1)-1}\nabla\Psi_k{}^{(0)}-\Psi_k{}^{(0)}\nabla\Psi_k{}^{*(1)-1}]\\&-\frac{e^2}{mc}\mathbf{a}_1\sum_k\Psi_k{}^{*(0)}\Psi_k{}^{(0)},\end{aligned} \tag{3.1}$$

and

$$\mathbf{j}_2=\mathbf{j}_2{}^{(L)}+\mathbf{j}_2{}^{(NL)}, \tag{3.2}$$

where

$$\begin{aligned}\mathbf{j}_2{}^{(L)}=-\frac{e\hbar}{2mi}\sum_k[&\Psi_k{}^{*(0)}\nabla\Psi_k{}^{(1)2}-\Psi_k{}^{(1)2}\nabla\Psi_k{}^{*(0)}\\&+\Psi_k{}^{*(1)-2}\nabla\Psi_k{}^{(0)}-\Psi_k{}^{(0)}\nabla\Psi_k{}^{*(1)-2}]\\&-\frac{e^2}{mc}\mathbf{a}_2\sum_k\Psi_k{}^{*(0)}\Psi_k{}^{(0)},\end{aligned} \tag{3.3}$$

and

$$\begin{aligned}\mathbf{j}_2{}^{(NL)}=-\frac{e\hbar}{2mi}\sum_k[&\Psi_k{}^{*(0)}\nabla\Psi_k{}^{(2)11}-\Psi_k{}^{(2)11}\nabla\Psi_k{}^{*(0)}\\&+\Psi_k{}^{*(2)-1-1}\nabla\Psi_k{}^{(0)}-\Psi_k{}^{(0)}\nabla\Psi_k{}^{*(2)-1-1}]\\&-\frac{e\hbar}{2mi}\sum_k[\Psi_k{}^{*(1)-1}\nabla\Psi_k{}^{(1)1}-\Psi_k{}^{(1)1}\nabla\Psi_k{}^{*(1)-1}]\\&-\frac{e^2}{mc}\mathbf{a}_1\sum_k[\Psi_k{}^{*(0)}\Psi_k{}^{(1)1}+\Psi_k{}^{*(1)-1}\Psi_k{}^{(0)}].\end{aligned} \tag{3.4}$$

Our approach has been quite general till now as far as the form of $V(\mathbf{x})$ is concerned. But in order to make use of this formulation for a real solid we will have to develop in future a proper approximation scheme to calculate $\mathbf{j}_1$ and $\mathbf{j}_2$. To facilitate this, we will first consider the simplest case with $V(\mathbf{x})=0$, and discuss how these results may be used for a finite metal. We will also consider briefly the case of bound electrons in crystals which lack inversion symmetry.

(A) Free-Electron Gas

When $V(\mathbf{x})=0$, the solution of Eq. (2.4) may be written as

$$\Psi_k{}^{(0)}\longrightarrow\Psi_{\mathbf{k}}{}^{(0)}=(2\pi)^{-3/2}e^{i\mathbf{k}\cdot\mathbf{x}}, \tag{3.5}$$

where

$$\sum_{\mathbf{k}}\Psi_{\mathbf{k}}{}^{*(0)}\Psi_{\mathbf{k}}{}^{(0)}=2\int_0^{k_{\mathrm{F}}}\frac{4\pi k^2dk}{(2\pi)^3}=n, \tag{3.6}$$

and where the unperturbed energy $E_{\mathbf{k}}$ is given by

$$E_{\mathbf{k}}=\hbar^2k^2/2m. \tag{3.7}$$

With an expansion

$$\mathbf{a}_1(\mathbf{x})=\sum_q a_1(q)e^{i\mathbf{q}\cdot\mathbf{x}}, \tag{3.8}$$

it is now possible to obtain from Eqs. (2.31), (3.1), (3.5), and (3.6) the Fourier transform $\mathbf{j}_1(\mathbf{q})$ of the current $\mathbf{j}_1(\mathbf{x})$ as[15]

$$\begin{aligned}\mathbf{j}_1(\mathbf{q})=\frac{e^2\hbar^2}{m^2c}(2\pi)^{-3}\sum_{\mathbf{k}}\Bigg[&\frac{(\mathbf{k}+\mathbf{q}/2)\{(\mathbf{k}+\mathbf{q}/2)\cdot\mathbf{a}_1(\mathbf{q})\}}{E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}-\hbar\omega}\\&+\frac{(\mathbf{k}-\mathbf{q}/2)\{(\mathbf{k}-\mathbf{q}/2)\cdot\mathbf{a}_1(\mathbf{q})\}}{E_{\mathbf{k}-\mathbf{q}}-E_{\mathbf{k}}+\hbar\omega}\Bigg]-\frac{e^2n}{mc}\mathbf{a}_1(\mathbf{q}).\end{aligned} \tag{3.9}$$

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[15] In Eq. (3.9) we may extend the summation over **k** to all states by introducing inside the summation sign the occupation numbers $n_{\mathbf{k}}$ which, at temperature $T=0$°K, is equal to 1 for $|\mathbf{k}|\leq k_{\mathrm{F}}$ and zero for $|\mathbf{k}|>k_{\mathrm{F}}$.

The macroscopic polarization $\mathbf{P}$ is given by

$$\partial \mathbf{P}/\partial t=\mathbf{J} \tag{3.10}$$

which leads to

$$\mathbf{P}_l=-\mathbf{j}_l/il\omega\,, \tag{3.11}$$

where

$$\mathbf{P}=\textstyle\sum_l \mathbf{P}_l e^{-il\omega t}. \tag{3.12}$$

In terms of the polarization $\mathbf{P}_1$ the linear transverse and longitudinal dielectric tensor may be defined in the usual way

$$[\boldsymbol{\varepsilon}(\mathbf{q},\omega)-1]\cdot\mathbf{a}_1=\frac{4\pi c}{i\omega}\mathbf{P}_1. \tag{3.13}$$

From Eqs. (3.8) and (3.10) we therefore obtain[16]

$$\boldsymbol{\varepsilon}^{\mathrm{long}}(\mathbf{q},\omega)=1-\frac{4\pi e^2 m}{\hbar^2 q^2}(2\pi)^{-3} \times\textstyle\sum_{\mathbf{k}}\left[\left(\frac{m\omega}{\hbar}-\mathbf{k}\cdot\mathbf{q}-q^2/2\right)^{-1} -\left(\frac{m\omega}{\hbar}+\mathbf{k}\cdot\mathbf{q}+q^2/2\right)^{-1}\right], \tag{3.14}$$

and

$$\boldsymbol{\varepsilon}^{\mathrm{tr}}(\mathbf{q},\omega)=1-\frac{\omega_p^2}{\omega^2}\frac{4\pi e^2}{m\omega^2 q^2}(2\pi)^{-3} \times\textstyle\sum_{\mathbf{k}}\left[\left(\frac{m\omega}{\hbar}-\mathbf{k}\cdot\mathbf{q}-q^2/2\right)^{-1} -\left(\frac{m\omega}{\hbar}+\mathbf{k}\cdot\mathbf{q}+q^2/2\right)^{-1}\right], \tag{3.15}$$

where

$$\omega_p=(4\pi ne^2/m)^{1/2}, \tag{3.16}$$

is the plasma frequency of the electrons.

Integrations over $\mathbf{k}$ in Eqs. (3.14) and (3.15) may be done in general to obtain the well-known results derived by Lindhard.[17] These integrations are, however, much simpler in the optical regions where the Fermi velocity $V_f\equiv\hbar\mathbf{k}_{\mathrm{F}}/m\ll\omega/q$, the velocity of light (long-wavelength approximation). In this case one finds the familiar results

$$\boldsymbol{\varepsilon}^{\mathrm{long}}(\mathbf{q},\omega)\simeq 1-(\omega_p^2/\omega^2)(1+\tfrac{3}{5}V_f^2q^2/\omega^2)\,, \tag{3.17}$$

and

$$\boldsymbol{\varepsilon}^{\mathrm{tr}}(\mathbf{q},\omega)\simeq 1-(\omega_p^2/\omega^2)(1+\tfrac{1}{5}V_f^2q^2/\omega^2)\,, \tag{3.18}$$

which may further be approximated to

$$\boldsymbol{\varepsilon}^{\mathrm{long}}\simeq\boldsymbol{\varepsilon}^{\mathrm{tr}}\simeq 1-\omega_p^2/\omega^2. \tag{3.19}$$

This leads to a simple expression for the current density which is given by

$$\mathbf{j}_1(\mathbf{x})=(-ne^2/mc)\mathbf{a}_1(\mathbf{x}). \tag{3.20}$$

An inspection of the expressions for $\mathbf{j}_1(\mathbf{x})$ and $\mathbf{j}_2^{(L)}(\mathbf{x})$ in Eqs. (3.1) and (3.3) shows that $\mathbf{j}_2^{(L)}(\mathbf{q})$ may be obtained from the expression for $\mathbf{j}_1(\mathbf{q})$ simply by replacing $\mathbf{a}_1(\mathbf{q})$ and ω by $\mathbf{a}_2(\mathbf{q})$ and 2ω, respectively. To find the bilinear second harmonic current $\mathbf{j}_2^{(NL)}$ let us assume that the solution of Eq. (2.37) gives $\mathbf{a}_1\sim e^{i\mathbf{q}_t\cdot\mathbf{x}}$. From Eqs. (2.31), (2.33), and (3.4)–(3.6) one therefore finds

$$\begin{aligned}\mathbf{j}_2^{(NL)}=&-(e^3n/2m^2c^2\omega)\mathbf{q}_t\mathbf{a}_1\cdot\mathbf{a}_1(1+(6/5)V_f^2q^2{}_t/\omega^2)\\&-(e^3n/2m^2c^2\omega)\mathbf{q}_t(\mathbf{q}_t\cdot\mathbf{a}_1)^2((12/5)(V_f^2/\omega^2))\\&-(e^3n/2m^2c^2\omega)\mathbf{a}_1(\mathbf{q}_t\cdot\mathbf{a}_1)(2+(12/5)(V_f^2q_t^2/\omega^2)),\end{aligned} \tag{3.21}$$

in the approximation where $V_f\ll\omega/q_t$. In the gauge-independent form, i.e., in terms of electromagnetic fields $\mathbf{E}_1$ and $\mathbf{H}_1$ the bilinear current is

$$\begin{aligned}\mathbf{j}_2^{(NL)}=&(e^3n/2m^2c\omega^2)(1+(6/5)V_f^2q_t^2/\omega^2)\mathbf{E}_1\times\mathbf{H}_1\\&+(e^3n/2m^2\omega^3)((12/5)(V_f^2/\omega^2))(\mathbf{E}_1\cdot\mathbf{q}_t)^2\mathbf{q}_t\\&+(e^3n/2m^2\omega^3)(3+(18/5)(V_f^2q_t^2/\omega^2))\mathbf{E}_1\mathbf{E}_1\cdot\mathbf{q}_t.\end{aligned} \tag{3.22}$$

Neglecting all the terms of the order $V_f^2q_t^2/\omega^2$ we may write[18]

$$\begin{aligned}\mathbf{j}_2^{(NL)}(\mathbf{x})=&(e^3n/2m^2c\omega^2)\mathbf{E}_1\times\mathbf{H}_1\\&-(ie^3/2m^2\omega^3)[n\mathbf{E}_1\cdot\boldsymbol{\nabla}\mathbf{E}_1+2\mathbf{E}_1\boldsymbol{\nabla}\cdot(n\mathbf{E}_1)].\end{aligned} \tag{3.23}$$

This model may be applied to a finite metal with a plane boundary with the following modifications. In the usual case when one excites only the transverse mode of the fundamental frequency in the solid, it may be seen from Eqs. (2.37) and (3.20) and the relation $\mathbf{E}_1=(i\omega/c)\mathbf{a}_1$ that

$$\boldsymbol{\nabla}\cdot\mathbf{E}_1=(4\pi e^2/m\omega^2)\boldsymbol{\nabla}\cdot(n\mathbf{E}_1). \tag{3.24}$$

From the solution[19] for the fundamental field it is also known that $\boldsymbol{\nabla}\cdot\mathbf{E}_1$ is zero inside the metal and may be taken as a delta function at the surface corresponding to the classical discontinuity of the normal component of $\mathbf{E}_1$ across the plane boundary. We may therefore again use an expression

$$\begin{aligned}\mathbf{j}_2^{(NL)}=&(-ie^3n/4m^2\omega^3)\boldsymbol{\nabla}(\mathbf{E}_1\cdot\mathbf{E}_1)\\&-(ie^3/m^2\omega^3)\mathbf{E}_1\boldsymbol{\nabla}\cdot(n\mathbf{E}_1),\end{aligned} \tag{3.25}$$

which is equivalent to Eq. (3.23), for a finite metal with the new interpretation of the second term as purely a surface term. From Eq. (3.24) and the fact that except for the normal component $\mathbf{E}_1\cdot\boldsymbol{\nabla}\mathbf{E}_1$ is zero, the above expression has the same form as Eq. (6.4) of I which was derived by using the Boltzmann equation for the distribution function of electrons. An equivalent form was used in another paper[20] by us where the predictions

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[16] While deriving these expressions one uses the identity that the summation over $\mathbf{k}$ for an odd function of $\mathbf{k}$ gives zero since $\sum_{\mathbf{k}} f(\mathbf{k})=\sum_{\mathbf{k}} f(-\mathbf{k})$. This symmetry has been used repeatedly in this paper.

[17] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **28**, 8 (1954).

[18] In Eq. (3.23) the second term on the right has been split in this particular form because $(c/i\omega)(\mathbf{E}_1\cdot\boldsymbol{\nabla}\mathbf{E}_1)$ term then cancels a corresponding term in $\mathbf{E}_1\times\mathbf{H}_1=(c/i\omega)\mathbf{E}_1\times(\boldsymbol{\nabla}\times\mathbf{E}_1)$. Usefulness of this form becomes more obvious while dealing with a finite metal.

[19] See Eqs. (4.7)–(4.13) and (4.19) of I.

[20] S. S. Jha, Phys. Rev. Letters **15**, 412 (1965).

of this theory were shown to be in good agreement with the experimental results of Brown, Parks, and Sleeper[21] for silver metal.

(B) Bound Electrons

Next let us consider $V(\mathbf{x})$ to be given by a periodic potential. The unperturbed states may now be taken as Bloch waves

$$\Psi_k^{(0)} \rightarrow \Psi_{b,\mathbf{k}}^{(0)} = N^{-1/2} U_b(\mathbf{x},k) e^{i\mathbf{k}\cdot\mathbf{x}}, \tag{3.26}$$

where b denotes the energy band and N is the number of cells in the crystal. In the dipole approximation[22] $\mathbf{a}_1(\mathbf{x})$ may be assumed to be constant within a cell. Considering only vertical interband transitions, the required matrix elements for calculating the current density become

$$\langle b'\mathbf{k}'|\xi_{1,2}|b,\mathbf{k}\rangle = \frac{e}{mc}\mathbf{a}_{1,2}\cdot\mathbf{p}_{b'\mathbf{k},b\mathbf{k}}\delta_{\mathbf{k},\mathbf{k}'} \tag{3.27}$$

and

$$\langle b'\mathbf{k}'|\eta_{11}|b,\mathbf{k}\rangle = 0 \quad \text{for} \quad b\neq b', \tag{3.28}$$

where

$$\mathbf{p}_{b'\mathbf{k},b\mathbf{k}} = -i\hbar\int_{\text{cell}} U_{b'}^*(\mathbf{x},\mathbf{k})\nabla U_b(\mathbf{x},\mathbf{k})\, d^3x \tag{3.29}$$

is the interband matrix element of the momentum operator.

Using the above equations and Eqs. (2.31), (2.32), and (3.4), an expression for the bilinear current density may be obtained. However, we will not write this complicated expression involving products of three momentum matrix elements because the result is essentially the same as obtained by Kelley.[23] Kelley has also shown in his paper that the solid considered cannot have inversion symmetry, since in that case a new set of states of definite parity can be chosen and the product of three momentum operators cannot connect states of the same parity. We are interested here in the order of magnitude of the induced field $\mathbf{E}_2$ only, and we have approximately[24]

$$|\mathbf{p}_{b'\mathbf{k},b\mathbf{k}}| \simeq \langle|\mathbf{p}|\rangle_{\mathrm{Av}}, \sim (m\hbar\omega)^{1/2} \tag{3.30}$$

in the optical region. With these considerations one obtains

$$|\mathbf{j}_2^{(NL)}| \sim \frac{e^3}{m^3c^2}\left(\frac{\langle p\rangle_{\mathrm{av}}}{\hbar}\right)^3 \frac{\langle p\rangle_{\mathrm{av}}^3}{\hbar^2\omega^2}|\mathbf{a}_1|^2, \tag{3.31}$$

which leads to

$$|\mathbf{a}_2| \sim \frac{e^3}{m^3c\hbar^2\omega^4}\left(\frac{\langle p\rangle_{\mathrm{av}}}{\hbar}\right)^3 \langle p\rangle_{\mathrm{av}}^3|\mathbf{a}_1|^2. \tag{3.32}$$

Using the estimate in Eq. (3.30) for $\langle p\rangle_{\mathrm{Av}}$, the second harmonic electric field may be written in the familiar form

$$|\mathbf{E}_2| = E_{\text{atomic}}^{-1}|\mathbf{E}_1|^2, \tag{3.33}$$

where

$$E_{\text{atomic}} \sim (e^2/r_0)(\hbar\omega/\mathcal{E}_{\mathrm{B}})^2, \tag{3.34}$$

and where r_0 is the Bohr radius and $\mathcal{E}_{\mathrm{B}}$ is the energy of the first Bohr orbit. Since $\hbar\omega \simeq \mathcal{E}_{\mathrm{B}}$ in the optical region, $E_{\text{atom}} \simeq 10^{-6}$–$10^{-7}$ esu.

4. SECOND-ORDER TRANSITION PROBABILITIES

In this section we will consider the process in which an electron jumps from a state k to a state n by absorption of either two photons of the fundamental frequency or one photon of the harmonic frequency. From Eqs. (2.25)–(2.29) the transition probability per unit time for such a process is found to be

$$\begin{aligned} W_{n,k} &= d/dt|C_{nk}^{(1)}(\text{term with } l=2) \\ &\qquad + C_{nk}^{(2)}(\text{terms with } l=l'=1)|^2 \\ &= \frac{2\pi}{\hbar}\left|\left\{\langle n|\xi_2|k\rangle + \langle n|\eta_{11}|k\rangle \right.\right. \\ &\qquad \left.\left. + \sum_m \frac{\langle n|\xi_1|m\rangle\langle m|\xi_1|k\rangle}{E_k - E_m + \hbar\omega}\right\}\right|^2 \\ &\qquad \times \delta(E_k + 2\hbar\omega - E_n), \end{aligned} \tag{4.1}$$

where we have used the identity

$$\lim_{\epsilon\to 0}\frac{\epsilon}{x^2+\epsilon^2} = \pi\delta(x). \tag{4.2}$$

In order to obtain the orders of magnitude of the first term in Eq. (4.1) which represents the contribution due to the harmonic field as compared to the second and third terms representing transitions of fundamental photons, let us consider these matrix elements in the dipole approximation. These are given by Eqs. (3.27) and (3.28) of Sec. 3. We thus obtain for the ratio of these two contributions

$$\frac{W_{nk}(2\omega)}{W_{nk}(\omega+\omega)} \sim \left(\frac{mc\hbar\omega}{e\langle\mathbf{p}\rangle_{\mathrm{av}}}\right)^2 \frac{|\mathbf{a}_2|^2}{|\mathbf{a}_1|^4}. \tag{4.3}$$

If one uses estimates for $\langle\mathbf{p}\rangle_{\mathrm{Av}}$ given by Eq. (3.30) and for $|\mathbf{a}_2|$ given by Eq. (3.32) one finds

$$\frac{W_{nk}(2\omega)}{W_{nk}(\omega+\omega)} \sim \frac{me^4}{2\hbar^3\omega} \sim 1, \tag{4.4}$$

for solids lacking inversion symmetry. This shows that for such solids we cannot neglect the harmonic-photon contributions on any *a priori* grounds.

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[21] F. Brown, R. E. Parks, and A. M. Sleeper, Phys. Rev. Letters **14**, 1029 (1965). See also: F. Brocon and R. E. Parks, *ibid.* **16**, 507 (1966).

[22] For more details about this model, see the paper by P. L. Kelley, J. Phys. Chem. Solids **24**, 1113 (1963).

[23] See Eq. (8) of Ref. (22).

[24] R. A. Smith, *Wave Mechanics of Crystalline Solids* (Chapman and Hall, Ltd., London, 1961), p. 409.

Now let us consider the second-order processes in solids with inversion symmetry. Here one knows that the induced harmonic field is zero in the dipole approximation and therefore is smaller by a factor $r_0\omega/c \simeq 10^{-2}$–$10^{-3}$ as compared to the case of solids lacking inversion symmetry. This immediately leads to the conclusion that in this case $W(2\omega)/W(\omega+\omega) \simeq 10^{-5}$, and we may safely neglect the harmonic photon contributions. For a specific case let us consider the second-order photoelectric effect[25] in metals. In our notation the second-order photocurrent is given by that part of $\mathbf{j}_2$ taken outside the metal, which is asymptotically nonvanishing at large distances from the metal and which is proportional to the fourth power in the incident field. The ratio of single-harmonic photon and double-fundamental-photon contributions to the current may be calculated for this case to be

$$\frac{j_0^{(\mathrm{Ph})}(2\omega)}{j^{(\mathrm{Ph})}(\omega+\omega)} \sim \left(\frac{\hbar\omega mc}{e^2}\right)^2 \frac{|\mathbf{a}_2|^2}{|\mathbf{a}_1|^4}, \qquad (4.5)$$

with the assumption that the depth of the surface potential well, the Fermi energy $\hbar^2/k_{\mathrm{F}}^2/2m$ and $\hbar\omega$ are all of the same order. By using Eqs. (3.21) and (2.37) one finds that for $q_t \sim \omega/c$,

$$|\mathbf{a}_2| \sim \frac{e^3 n}{m^2 c^2 \omega^2} |\mathbf{a}_1|^2 \qquad (4.6)$$

in metals. Equations (3.6), (4.5), and (4.6) then lead to

$$\frac{j_0^{(\mathrm{Ph})}(2\omega)}{j_0^{(\mathrm{Ph})}(\omega+\omega)} \sim \left(\frac{e^2}{\hbar c}\right)^2 \left(\frac{\hbar^2 k_{\mathrm{F}}^2}{2m\hbar\omega}\right)^4 \sim \left(\frac{e^2}{\hbar c}\right)^2 \simeq 10^{-5}, \qquad (4.7)$$

for

$$\hbar\omega \sim \frac{\hbar^2 k_{\mathrm{F}}^2}{2m}.$$

Actually we have dealt with only the second-order optical absorption in this section but it is quite clear that these arguments may also be extended to the second-order emission.

5. CONCLUSIONS

We obtained the self-consistent expressions for the second-order optical transition probabilities of the electrons in a solid, by first considering the nature of induced fields in the solid. We then showed that the single-photon transition probability due to the second-harmonic field produced in a solid lacking inversion symmetry, is comparable to the double-photon transition probability due to the induced fundamental field. In centrosymmetric metals it was shown that the contribution due to the former process was smaller by a factor $(e^2/\hbar c)^2$ than the latter and therefore could be neglected. Although our results for the case of a general solid lacking inversion symmetry were obtained by using crude estimates for the interband momentum matrix elements, which may at best be considered to be a dimensional analysis, we would like to stress here that our conclusions are based essentially on the following general arguments. In the long-wavelength approximation, in a solid lacking inversion symmetry, the bilinear polarizability and hence the second-harmonic field is greater by a factor $c/r_0\omega$ (r_0 is the atomic radius) as compared to centrosymmetric solids. Hence the single second-harmonic photon transition probability is greater by a factor $(c/r_0\omega)^2$ as compared to metals. This effectively cancels the factor of the order $(e^2/\hbar c)^2$ obtained for metals, in the optical region where $\hbar\omega \sim me^4/\hbar^2$.

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[25] For details about the usual model taken for this effect in metals, see R. E. B. Makinson and M. J. Buckingham, Proc. Phys. Soc. (London) **64A**, 135 (1951); I. Adawi, Phys. Rev. **134**, A778 (1964).