Estimates of the saturated magnetic remanence at 0°K were obtained by fitting the low-temperature remanence data to paramagnetic expressions. The resulting estimates corresponded to a few percent of the available total moment of the solute atoms.

The magnetic transitions did not occur in Co and V alloys of 1 at.% concentration. These alloys also did not exhibit a Curie-Weiss law. The occurrence of the transition in the case of Cr, Mn, and Fe does not follow uniquely from the particular form of magnetic transition exhibited at higher concentrations. Instead the properties of the transition appear to be a general consequence of dilution in those alloys for which the transition-metal impurities exhibit strong paramagnetism.

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Nonlinear Optical Theory in Solids

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We use a simple rule giving the expectation value of a quantum operator for any perturbation order to calculate the general second-order conductivity tensor of a solid. The expression for the conductivity tensor amounts to a regrouping of terms in the conventional expressions and takes a considerably simplified form. The formula is applied to second harmonic generation in a free-electron gas and reduces to the classical equation given by Kronig and Boukema in the optical region. The second harmonic radiation generated in metals is shown to possess two resonances occuring at the plasma oscillation frequency for p polarization and at half the plasma frequency for p and s polarization. The amplitude of the resonance is related to the imaginary part of the dielectric constant at the plasma frequency, $\epsilon_2(\omega_p)$. Only metals with $\epsilon_2(\omega_p)\ll 1$ (i.e., alkali metals, Ag and Al) will show resonant effects.

1. INTRODUCTION

THE quantum-mechanical treatment of second harmonic generation has been considered by many authors.[1,2] As the conventional calculation for the second-order conductivity involves much algebraic complexity, and the expression obtained contains many terms, the formula has been studied in detail only in the dipole approximation.

Instead of following the conventional procedure, we make use of a rule which gives the expectation value of a quantum operator for any perturbation order.[3] Our expression for the conductivity tensor amounts to a regrouping of terms in the conventional expression and takes a simplified form.[3a] We next apply this formula to the study of second harmonic generation in a free-electron gas and find that in the optical region, the second-order conductivity tensor agrees with the classical form,[4] which is of the same order of magnitude as the experimentally observed second-order conductivity tensor of some solids like KDP, which lack inversion symmetry. The second harmonic radiation generated in metals is shown to possess two resonances, occurring at the plasma oscillation frequency and half the plasma oscillation frequency which arise from the resonance of the plasma oscillation with the fundamental and the second harmonic radiation, respectively. These resonance effects further enhance the possibility of large second harmonic production in metals.

2. THE CONDUCTIVITY TENSOR

Let us consider the interaction of an electromagnetic field with a system which is originally described by a Hamiltonian H_0. In a solid H_0 will be the kinetic energy plus a periodic potential. The interaction Hamiltonian is

$$H'=-\frac{e}{2mc}[\mathbf{A}(x,t)\cdot\mathbf{p}+\mathbf{p}\cdot\mathbf{A}(x,t)]+\frac{e^2}{2mc^2}A^2(x,t), \quad (1)$$

where $\mathbf{A}(x,t)$ is the vector potential for the electromagnetic field, the gauge being chosen so that the scalar potential is zero and $\mathbf{p}=-ih\nabla$. Denoting C_s^+ and C_s as the electron creation and annihilation operator of state s, which is an eigenstate of the unperturbed Hamiltonian

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[1] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).

[2] P. N. Butcher and T. P. McLean, Proc. Phys. Soc. (London) **81**, 219 (1962).

[3] Hung Cheng (to be published).

[3a] *Note added in proof.* A similar formalism has also been used by P. L. Kelley, Phys. Chem. Solids **24**, 607 (1963); **24**, 1113 (1963).

[4] R. Kronig and J. I. Boukema, Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B **66**, 8 (1963).

H_0, we obtain in the interaction representation,

$$H'(t)=e^{iH_0t}H'e^{-iH_0t}$$
$$=\sum_{ss'}\frac{-e}{2mc}(\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p})_{ss'}C_s^+C_{s'}e^{-i\omega_{s's}t}+\frac{e^2}{2mc^2}[A^2(x,t)]_{ss'}\cdot C_s^+C_{s'}e^{-i\omega_{s's}t}, \quad (2)$$

where $\omega_{s's}=(1/\hbar)(E_{s'}-E_s)$. If we decompose $H'(t)$ in a Fourier series,

$$H'(t)=\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}e^{-i\omega' t}H'(\omega'), \quad (3)$$

then from (2) and (3) we obtain

$$H'(\omega)=\frac{-e}{2mc}\sum_{s,s'}[\mathbf{A}(\mathbf{x},\omega-\omega_{s's})\cdot\mathbf{p}+\mathbf{p}\cdot\mathbf{A}(\mathbf{x},\omega-\omega_{s's})]_{ss'}C_s^+C_{s'}+\sum_{s,s'}\frac{e^2}{2mc^2}\left[\int\mathbf{A}(x,\omega')\cdot\mathbf{A}(x,\omega-\omega'-\omega_{s's})\frac{d\omega'}{2\pi}\right]_{ss'}C_s^+C_{s'}, \quad (4)$$

where $\mathbf{A}(\mathbf{x},\omega)$ is the Fourier transform of $\mathbf{A}(\mathbf{x},t)$,

$$\mathbf{A}(\mathbf{x},t)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\mathbf{A}(\mathbf{x},\omega)e^{-i\omega t}.$$

The current operator $j_\alpha(\mathbf{x},t)$ of the system in the interaction representation is given by

$$j_\alpha(\mathbf{x},t)=\frac{e}{2m}\sum_{rr'}[\psi_{r'}^*(\mathbf{x})p_\alpha\psi_r(\mathbf{x})-\psi_r(\mathbf{x})p_\alpha\psi_{r'}^*(\mathbf{x})]C_{r'}^+C_re^{-i\omega_{rr'}t}-\frac{e^2}{mc}A_\alpha(\mathbf{x},t)\sum_{r,r'}\psi_{r'}^*(\mathbf{x})\psi_r(\mathbf{x})C_{r'}^+C_re^{-i\omega_{rr'}t}. \quad (5)$$

Define

$$j_\alpha(\mathbf{x},t)=\int j_\alpha(\mathbf{Q},\omega)e^{-i\omega t}\exp(i\mathbf{Q}\cdot\mathbf{x})d\omega d^3\mathbf{Q}/(2\pi)^4, \quad (6)$$

then we obtain from (5) and (6) that

$$j_\alpha(\mathbf{Q},\omega)=\frac{e}{2m}\sum_{rr'}[\exp(-i\mathbf{Q}\cdot\mathbf{x})p_\alpha+p_\alpha\exp(-i\mathbf{Q}\cdot\mathbf{x})]_{r'r}C^+_{r'}C_r2\pi\delta(\omega-\omega_{rr'})-\frac{e^2}{mc}\sum_{rr'}[A_\alpha(\mathbf{x},\omega-\omega_{rr'})\exp(-i\mathbf{Q}\cdot\mathbf{x})]_{r'r}C^+_{r'}C_r. \quad (7)$$

The expectation value of the current operator is given by[3]

$$\bar{j}_\alpha(\mathbf{x},t)\equiv\langle\psi_I(t)|j_\alpha(\mathbf{x},t)|\psi_I(t)\rangle$$
$$=\langle\psi_I(-\infty)|j_\alpha(\mathbf{x},t)+(-1)\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\frac{[H'(\omega_1),j_\alpha(\mathbf{x},t)]}{\hbar\omega_1+i\epsilon}e^{-i\omega_1t}+(-1)^2\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}\frac{[H'(\omega_1)[H'(\omega_2),j_\alpha(\mathbf{x},t)]]e^{-i(\omega_1+\omega_2)t}}{(\hbar\omega_1+i\epsilon)(\hbar\omega_1+\hbar\omega_2+i\epsilon)}+\cdots|\psi_I(-\infty)\rangle, \quad (8)$$

where $\psi_I(t)$ is the wave function of the system in the interaction representation and ϵ is an infinitesimal quantity.

Decomposing $\bar{j}_\alpha(\mathbf{x},t)$ into Fourier components,

$$\bar{j}_\alpha(\mathbf{Q},\omega)=\int\bar{j}_\alpha(\mathbf{x},t)\exp(i\omega t-i\mathbf{Q}\cdot\mathbf{x})dtd^3x, \quad (9)$$

we obtain from (8) and (9)

$$\vec{j}_\alpha(\mathbf{Q},\omega)=\langle\psi_I(-\infty)|\,j_\alpha(\mathbf{Q},\omega)+(-1)\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\frac{[H'(\omega_1),\,j_\alpha(\mathbf{Q},\,\omega-\omega_1)]}{h\omega_1+i\epsilon}$$
$$+(-1)^2\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}\frac{[H'(\omega_1),\,[H'(\omega_2),\,j_\alpha(\mathbf{Q},\,\omega-\omega_1-\omega_2)]]}{(h\omega_1+i\epsilon)(h\omega_1+h\omega_2+i\epsilon)}+\cdots|\psi_I(-\infty)\rangle. \quad (10)$$

Substituting (4) and (7) into (10), and retaining only the terms quadratic in A, we get

$$\vec{j}_\alpha^{(2)}(\mathbf{Q},\omega)=-\frac{e^3}{m^2c^2}\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\sum_{ss'}\Bigg\{\frac{[\mathbf{A}(\mathbf{x},\omega_1)\cdot\mathbf{p}+\mathbf{p}\cdot\mathbf{A}(\mathbf{x},\omega_1)]_{ss'}[\exp(-i\mathbf{Q}\cdot\mathbf{x})A_\alpha(\mathbf{x},\,\omega-\omega_1)]_{s's}}{2\hbar(\omega_1+\omega_{ss'})}$$
$$+\frac{1}{4}\frac{[\mathbf{A}(\mathbf{x},\omega_1)\cdot\mathbf{A}(\mathbf{x},\,\omega-\omega_1)]_{ss'}}{\hbar(\omega-\omega_{ss'})}[\exp(-i\mathbf{Q}\cdot\mathbf{x})p_\alpha+p_\alpha\exp(-i\mathbf{Q}\cdot\mathbf{x})]_{s's}\Bigg\}(f_s-f_{s'})$$
$$+\frac{e^3}{8m^3c^2}\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\frac{1}{\hbar\omega_1}\sum_{ss'r'}[\mathbf{A}(\mathbf{x},\,\omega-\omega_1-\omega_{s'r'})\cdot\mathbf{p}+\mathbf{p}\cdot\mathbf{A}(\mathbf{x},\,\omega-\omega_1-\omega_{s'r'})]_{ss'}$$
$$\times[\exp(-i\mathbf{Q}\cdot\mathbf{x})p_\alpha+p_\alpha\exp(-i\mathbf{Q}\cdot\mathbf{x})]_{r's}[\mathbf{A}(\mathbf{x},\,\omega_1-\omega_{r's'})\cdot\mathbf{p}+\mathbf{p}\cdot\mathbf{A}(\mathbf{x},\,\omega_1-\omega_{r's'})]_{s'r'}$$
$$\times(f_{r'}-f_{s'})/(\hbar\omega-\hbar\omega_{sr'})+\text{complex conjugate of last term with } Q\to-Q,\ \omega\to-\omega. \quad (11)$$

In (11) f_s is the occupation number of state s.

We define the second-order conductivity tensor by the formula

$$\vec{j}_\alpha^{(2)}(\mathbf{Q},\omega)=\int\sigma_{\alpha\beta\gamma}^{(2)}(q_1,\,Q-q_1;\,\omega_1,\,\omega-\omega_1)E_\beta(q_1,\omega_1)E_\gamma(Q-q_1,\,\omega-\omega_1)\frac{d^3q_1d\omega_1}{(2\pi)^4}. \quad (12)$$

Since in a solid, an arbitrary translation does not leave the crystal invariant, such a definition is possible only when umklapp processes, which give rise to local-field corrections,[5] are neglected. In this approximation, the symmetrized conductivity tensor is given from (11) and (12) by

$$\sigma_{\alpha\beta\gamma}^{(2)}(q_1,q_2;\,\omega_1,\omega_2)$$
$$=\frac{e^3}{2m^2\omega_1\omega_2}\sum P(\beta,q_1,\omega_1;\,\gamma,q_2,\omega_2)\Bigg\{\sum_{n'\,n\,\mathbf{k}}\Bigg[\langle n,\mathbf{k}|-ih\nabla_\beta+hk_\beta-\frac{\hbar q_{1\beta}}{2}|n',\,\mathbf{k}-\mathbf{q}_1\rangle$$
$$\times\langle n',\,\mathbf{k}-\mathbf{q}_1|\,n,\mathbf{k}\rangle\frac{\delta\gamma\alpha(f_{n,\mathbf{k}}-f_{n',\mathbf{k}-\mathbf{q}})}{[h\omega_1+E_{n'}(\mathbf{k}-\mathbf{q}_1)-E_n(\mathbf{k})+i\epsilon]}+\frac{1}{2}\frac{\langle n,\mathbf{k}|\,n',\,\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2\rangle}{[h\omega_1+h\omega_2-E_n(\mathbf{k})+E_{n'}(\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2)+i\epsilon]}$$
$$\times\langle n',\,\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2|-ih\nabla_\alpha+hk_\alpha-\frac{\hbar q_{1\alpha}+\hbar q_{2\alpha}}{2}|\,n,k\rangle\delta_{\beta\gamma}\cdot(f_{n,\mathbf{k}}-f_{n',\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2})\Bigg]$$
$$-\frac{1}{m}\sum_{n,n',n'',\mathbf{k}}\langle n,\mathbf{k}|-ih\nabla_\beta+hk_\beta-\frac{\hbar q_{1\beta}}{2}|n',\,\mathbf{k}-\mathbf{q}_1\rangle\langle n',\,\mathbf{k}-\mathbf{q}_1|-ih\nabla_\gamma+hk_\gamma-hq_{1\gamma}-\frac{\hbar q_{2\gamma}}{2}|n'',\,\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2\rangle$$
$$\cdot\langle n'',\,\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2|-ih\nabla_\alpha+hk_\alpha-\frac{\hbar(q_{1\alpha}+q_{2\alpha})}{2}|\,n,\mathbf{k}\rangle$$
$$\times\frac{(f_{n'',\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2}-f_{n',\mathbf{k}-\mathbf{q}_1})}{[\hbar\omega_2-E_{n'}(\mathbf{k}-\mathbf{q}_1)+E_{n''}(\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2)+i\epsilon][\hbar\omega_1+\hbar\omega_2-E_n(\mathbf{k})+E_{n''}(\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2)+i\epsilon]}$$
$$+\text{c.c. of last term with } \omega_2\to-\omega_2,\ \omega_1\to-\omega_1,\ q_1\to-q_1,\ q_2\to-q_2\Bigg]\Bigg\}, \quad (13)$$

[5] Stephen Adler, Phys. Rev. **126**, 413 (1962).

where P stands for the permutation symbol and $E_n(\mathbf{k})$ for the energy of the Bloch state in band n with wave vector $\mathbf{k}$. In (13), all matrix elements are taken with respect to the periodic part of the Bloch wave functions $u_{n,\mathbf{k}}(r)$:

$$\langle n,\mathbf{k}|O|n',\mathbf{k}'\rangle\equiv\frac{1}{v_a}\int u_{n,\mathbf{k}}{}^*(\mathbf{x})Ou_{n',\mathbf{k}'}(\mathbf{x})d^3x, \quad (14)$$

where the integration is over a unit cell and v_a denotes its volume.

The expression (11) may be compared with the second-order polarization given by Armstrong *et al.*,[1] and is seen to be considerably more compact. In the dipole approximation ($q_1, q_2, \to 0$), the first two terms on the right-hand side of (13) vanish, and the expression is equivalent but more compact than that given by Butcher and McLean.[2] For the calculation of the third and higher order conductivity tensors, the advantages of the present method will become even greater.

3. SECOND HARMONIC GENERATION BY A FREE-ELECTRON GAS

In this section, we turn to the application of Eq. (13) to the free-electron gas. The classical result has been given by Kronig and Boukema,[4] and our quantum result reduces to it in the optical region where nonlocal effects are negligible.

We consider a transverse electromagnetic wave incident on the plane boundary of a metal in the free-electron approximation. The fundamental wave in the metal is then transverse and the conductivity tensor becomes

$$\sigma_{\alpha\beta\gamma}(q_1,q_2;\omega_1,\omega_2)=\frac{e^3}{2m^2\omega_1\omega_2}\sum P(\beta q_1\omega_1,\gamma q_2\omega_2)\cdot\Bigg[\int 2\frac{d^3k}{(2\pi)^3}\Bigg[k_\beta/\left(\omega_1-\frac{\hbar\mathbf{k}\cdot\mathbf{q}_1}{m}+\frac{\hbar q_1{}^2}{2m}\right)\delta\gamma\alpha(f_\mathbf{k}-f_{\mathbf{k}-\mathbf{q}_1})$$
$$+\frac{1}{4}\frac{(2k_\alpha-q_{1\alpha}-q_{2\alpha})\delta_{\beta\gamma}(f_\mathbf{k}-f_{\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2})}{\omega_1+\omega_2-[\hbar\mathbf{k}\cdot(\mathbf{q}_1+\mathbf{q}_2)/m]+[\hbar(\mathbf{q}_1+\mathbf{q}_2)^2/2m]}$$
$$-\frac{\hbar}{2m}\frac{k_\beta k_\gamma(2k_\alpha-q_{1\alpha}-q_{2\alpha})(f_{\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2}-f_{\mathbf{k}-\mathbf{q}_1})}{\left[\omega_2-\hbar\frac{\mathbf{k}\cdot\mathbf{q}_2}{m}-\frac{\hbar q_1{}^2}{2m}+\frac{\hbar(\mathbf{q}_1+\mathbf{q}_2)^2}{2m}\right]\left[\omega_1+\omega_2-\frac{\hbar\mathbf{k}\cdot(\mathbf{q}_1+\mathbf{q}_2)}{m}+\frac{\hbar(\mathbf{q}_1+\mathbf{q}_2)^2}{2m}\right]}$$
$$+\text{c.c. of last term with } q_1,\ q_2,\ \omega_1,\ \omega_2\to -q_1,\ -q_2,\ -\omega_1,\ -\omega_2\Bigg]\Bigg]. \quad (15)$$

In the optical region, the inequalities

$$\omega_1\gg\hbar\frac{\mathbf{k}\cdot\mathbf{q}_1}{m},\ \frac{\hbar q_1{}^2}{2m}$$

show that nonlocal effects are negligible. The conductivity given by Eq. (15) becomes approximately equal to

$$\sigma_{\alpha\beta\gamma}(q_1,q_2;\omega_1,\omega_2)=-\frac{e^3N(q_1{}^\alpha+q_2{}^\alpha)}{2m^2\omega_1\omega_2(\omega_1+\omega_2)}\delta_{\beta\gamma}, \quad (16)$$

where N is the total number of electrons per unit volume. Equation (16) agrees with the classical result. Although the right-hand side of (16) vanishes in the dipole approximation ($q_1, q_2\to 0$), in the optical region it is of the same order of magnitude as the conductivity tensor of a solid lacking inversion symmetry such as KDP, as measured by Ashkin *et al.*[6] This is probably due to the fact that the inversion symmetry is not strongly violated for such materials. Although the conductivity tensor of the metal is comparable in magnitude to KDP, the polarization is also proportional to the energy of the transmitted fundamental which for metals is usually small in the optical region.

To calculate the second harmonic generation by a fundamental wave of angular frequency ω incident on a metal, we need to solve the Maxwell equations with appropriate boundary conditions. The general solution has been given by Bloembergen and Pershan,[7] and Kronig and Boukema have treated the boundary condition for the nonlinear metal.[4] The result is that the harmonic wave in the metal is given by

$$\mathbf{E}_2=\mathbf{e}_T\mathcal{E}_2\exp(i\mathbf{k}_2\cdot\mathbf{x}-2i\omega t)$$
$$+\frac{4\pi\mathbf{k}_{1T}}{\omega\epsilon(2\omega)}\mathcal{E}_{1T}{}^2\alpha(\omega)\exp(2i\mathbf{k}_{1T}\cdot\mathbf{x}-2i\omega t), \quad (17)$$

where $\mathbf{k}_2$ is the wave vector of the homogeneous wave of frequency 2ω and $\mathcal{E}_{1T}$, $\mathbf{k}_{1T}$ refers to the amplitude and wave vector of the transmitted fundamental. The function $\alpha(\omega)$ is found from Eq. (16) to be

$$\alpha(\omega)=-e^3N/4m^2\omega^3 \quad (18)$$

[6] A. Ashkin, G. D. Boyd, and J. M. Dziedzic, Phys. Rev. Letters **11**, 14 (1963).

[7] N. Bloembergen and P. S. Pershan, Phys. Rev. **126**, 606 (1962).

and $\epsilon(\omega)$ is the dielectric constant of the metal. The amplitude $\mathcal{E}_2$ is given by

$$\mathcal{E}_2=\frac{-(4\pi/c)\mathcal{E}_{1T}{}^2\alpha(\omega)\sin\theta_i}{\epsilon(2\omega)[\epsilon^{1/2}(2\omega)\cos\theta_i+\cos\theta_{2T}]}, \tag{19}$$

where θ_i is the angle of incidence. The reflected harmonic amplitude $\mathcal{E}_2{}^R$ is given by $\mathcal{E}_2[\epsilon(2\omega)]^{1/2}$.

We define the angles

$$\sin\theta_{1T}=\frac{\sin\theta_i}{[\epsilon(\omega)]^{1/2}}, \quad \sin\theta_{2T}=\frac{\sin\theta_i}{[\epsilon(2\omega)]^{1/2}}, \tag{20}$$

then when the incident wave of amplitude $\mathcal{E}_i$ is p polarized (s polarized) the amplitude $\mathcal{E}_{1T}{}^{p,s}$ is given by

$$\begin{aligned}\frac{\mathcal{E}_{1T}{}^p}{\mathcal{E}_i}&=\frac{2\cos\theta_i}{\epsilon^{1/2}(\omega)\cos\theta_i+\cos\theta_{1T}},\\ \frac{\mathcal{E}_{1T}{}^s}{\mathcal{E}_i}&=\frac{2\cos\theta_i}{\cos\theta_i+\epsilon^{1/2}(\omega)\cos\theta_{1T}}.\end{aligned} \tag{21}$$

Equations (19)–(21) are also valid for damped waves when the angles become complex.

To examine resonant phenomena we separate the dielectric constant into real and imaginary parts

$$\epsilon(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega) \tag{22}$$

and define a plasma frequency ω_p by $\epsilon_1(\omega_p)=0$. When the fundamental frequency is near ω_p a resonance in both the reflected and transmitted harmonic amplitudes will occur near normal incidence for p polarization. Consider the frequency dependence of $\mathcal{E}_2$ at an angle $\theta_i\ll 1$ given by

$$\sin^2\theta_i{}^2=\epsilon_1(\omega), \tag{23}$$

then (19) gives

$$\mathcal{E}_2=-\frac{4\pi}{c}\frac{\alpha(\omega_p)}{\epsilon(2\omega_p)}\frac{4}{[\epsilon^{1/2}(2\omega_p)+\cos\theta_{2T}]}\times\frac{[\epsilon_1(\omega)]^{1/2}\mathcal{E}_i{}^2}{\{[\epsilon_1(\omega)+i\epsilon_2(\omega)]^{1/2}+[i\epsilon_2(\omega)/\epsilon_1(\omega)+i\epsilon_2(\omega)]^{1/2}\}^2}. \tag{24}$$

Resonant effects will occur only for those metals for which $\epsilon_2(\omega_p)\ll 1$. These include the alkali metals,[8] Ag,[9] and Al.[10] The contribution to ϵ_2 arises primarily from interband transitions.[9,10] Then in the frequency region where $(\epsilon_2)^{1/2}\leq\epsilon_1\ll 1$, $\mathcal{E}_2$ and $\mathcal{E}_2{}^R$ have the form

$$\mathcal{E}_2\sim[\epsilon_1(\omega)]^{-1/2}; \quad \mathcal{E}_2{}^R\sim[\epsilon_1(\omega)]^{-1/2}. \tag{25}$$

Thus the size of the resonance is determined by $\epsilon_2{}^{-1/4}$ and occurs near normal incidence. However at normal incidence ($\theta_i=0$) no second harmonic is generated.

When the harmonic frequency 2ω is near the plasma frequency a resonance occurs for both s and p polarization. If we consider an angle of incidence defined by $\sin^2\theta_i=\epsilon_1{}^{1/2}(2\omega)$, a similar analysis shows that in the range $(\epsilon_2)^{1/2}\leq\epsilon_1\ll 1$, $\mathcal{E}_2$ and $\mathcal{E}_2{}^R$ have the form

$$\mathcal{E}_2\sim[\epsilon_1(2\omega)]^{-1}; \quad \mathcal{E}_2{}^R\sim[\epsilon_1(2\omega)]^{-1/2} \tag{26}$$

so that the size of the resonance is determined by $[\epsilon_2(\omega_p)]^{-1/2}$ and $[\epsilon_2(\omega_p)]^{-1/4}$, respectively.

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[8] H. E. Ives and H. B. Briggs, J. Opt. Soc. Am. **26**, 238 (1936); **27**, 181, 395 (1937).
[9] H. Ehrenreich and H. R. Philipp, Phys. Rev. **128**, 1622 (1962).
[10] H. Ehrenreich, H. R. Philipp, and B. Segall (to be published).