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Nonlinearities in metals

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Optical Nonlinearities in Metals

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Nonlinearities in Metals

- A reasonable elementary model for a metal is an isotropic free electron gas. A consequence of this is that metals are opaque to visible radiation. For frequencies lower than the plasma frequency, the electromagnetic radiation can penetrate only for a small depth (skin depth) of the order of the wavelength and due to their symmetry, bulk metals lack of dipole sources for second harmonic production.

Nonlinearities in Metals

Within the skin depth of the incident electromagnetic field, there are, however, Lorentz forces on free (and to some degree also bound) electrons, as well as interband transitions, both of which lead to nonlinear bulk magnetic dipole polarization sources.

Nonlinearities in Metals

. Further, the breaking of inversion symmetry and the large change in dielectric constant at the metal-vacuum interface introduces strong surface currents within a few Fermi wavelengths of the surface which produce electric quadrupole terms. These mechanisms are however very weak. This not withstanding second harmonic generation from the surface of metals was studied since the beginning.

Nonlinearities in metals

- In metals bulk production of dipole second harmonic radiation is inhibited due to symmetry reasons and only an electric quadrupole and a magnetic dipole terms may be active
- These reasons do not exhist at surface due to the lack of symmetry in a sheet region of the order of a few Å's thickness between vacuum and the metal. In this case the discontinuity of the electric field is important
- Therefore SHG, although has a very low efficiency (~10^{-10}) is used as a surface probe.

Nonlinearities in metals

Free electron gas theory

The equation of motion for a free electron is

$$\frac{d^2\mathbf{r}}{dt^2} = -\frac{e}{m}\left(\mathbf{E} + \frac{1}{c}\mathbf{v}\times\mathbf{B}\right) \qquad (1)$$

Damping is neglected for simplicity.

Clearly, the only nonlinear term in this equation is the Lorentz force term. Since v << c in a plasma, the Lorentz force is much weaker than the Coulomb force, and then (e/mc)$\mathbf{v}\times\mathbf{B}$ in (1) can be treated as a perturbation in the successive approximation of the solution.

For $\mathbf{E} = \mathbf{E}_1 e^{ik_1 \cdot r - i\omega_1 t} + \mathbf{E}_2 e^{ik_2 \cdot r - i\omega_2 t}$ + c.c., we obtain

$$\mathbf{r}^{(1)}(\omega_i) = \frac{\mathrm{e}}{\mathrm{m}\omega_{\mathrm{i}}^2} \mathbf{E}_i e^{ik_1 \cdot r^{(0)} - i\omega_1 t} + c.c.$$

$$\mathbf{r}^{(2)}(\omega_1 + \omega_2) = \frac{-ie^2}{m^2 \omega_1 \omega_2 (\omega_1 + \omega_2)^2} \times \left[\mathbf{E}_1 \times (k_2 \times \mathbf{E}_2) + \mathbf{E}_2 \times (k_1 \times \mathbf{E}_1) \right] \times e^{i(k_1 + k_2) \cdot r^{(0)} - i(\omega_1 + \omega_2)t} + c.c. \qquad (2)$$

,

and so on.

For a uniform plasma with an electronic charge density ρ, the current density is given by

$$\mathbf{J} = \mathbf{J}^{(1)} + \mathbf{J}^{(2)} + \cdots$$

$$= \rho \frac{\partial}{\partial t}\left(\mathbf{r}^{(1)} + \mathbf{r}^{(2)} + \cdots\right) \qquad (3)$$

with, for example,

$$\mathbf{J}^{(2)}(\omega_1 + \omega_2) = \rho \frac{\partial}{\partial t}\mathbf{r}^{(2)}(\omega_1 + \omega_2)$$

In a more rigorous treatment, we must also take into account the spatial variations of the electron density ρ and velocity v. Two equations, the equation of motion and the continuity equation, are now necessary to describe the electron plasma:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{v} = -\frac{\nabla p}{m\rho} - \frac{e}{m}\left(\mathbf{E} + \frac{1}{c}\mathbf{v} \times \mathbf{B}\right)$$

and

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \qquad (4)$$

where p is the pressure and m is the electron mass.

The pressure gradient term in the equation of motion is responsible for the dispersion of plasma resonance, but in the following calculation we assume $\nabla p = 0$ for simplicity.

Then, coupled with (4), is the set of Maxwell's equations

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t},$$

$$\nabla \times \mathbf{B} - \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} = \frac{4\pi \mathbf{J}}{c} = \frac{4\pi \rho \mathbf{v}}{\mathrm{c}}, \qquad (5)$$

$$\nabla \cdot \mathbf{E} = 4\pi\left(\rho - \rho^{(0)}\right),$$

and

$$\nabla \cdot \mathbf{B} = 0$$

We assume here that there is a fixed positive charge background in the plasma to assure charge neutrality in the absence of external perturbation. Successive approximation can be used to find **J** as a function of E from (4) and (5). Let

$$\rho = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + \cdots,$$

$$\mathbf{v} = \mathbf{v}^{(1)} + \mathbf{v}^{(2)} + \cdots,$$

and

$$\mathbf{j} = \mathbf{j}^{(1)} + \mathbf{j}^{(2)} + \cdots \qquad (6)$$

with

$$\mathbf{j}^{(1)} = \rho^{(0)}\mathbf{v}^{(1)}$$

and

$$\mathbf{j}^{(2)} = \rho^{(0)}\mathbf{v}^{(2)} + \rho^{(1)}\mathbf{v}^{(1)} \qquad (7)$$

We shall find the expression for $\mathbf{j}^{(2)}(2\omega)$ as an example assuming

$$\mathbf{E} = \mathbf{E} \times \exp\left(i\mathbf{k}\cdot\mathbf{r} - i\omega t\right).$$

Substitution of (6) into (4) and (5) yields

$$\frac{\partial \mathbf{v}^{(1)}(\omega)}{\partial t} = -i\omega\mathbf{v}^{(1)} = -\frac{e}{m}\mathbf{E},$$

$$\frac{\partial \rho^{(1)}(\omega)}{\partial t} = -i\omega\rho^{(1)} = -\nabla\cdot\left(\rho^{(0)}\mathbf{v}^{(1)}\right)$$

$$\nabla\cdot\mathbf{E} = 4\pi\rho^{(1)}(\omega),$$

$$\frac{\partial \mathbf{v}^{(2)}(2\omega)}{\partial t} = -i2\omega\mathbf{v}^{(2)} = -\left(\mathbf{v}^{(1)}\cdot\nabla\right)\mathbf{v}^{(1)} - \frac{e}{mc}\mathbf{v}^{(1)}\times\mathbf{B} \qquad (8)$$

The second-order current density is then given by

$$\mathbf{J}^{(2)}(2\omega) = \frac{i\rho^{(0)}}{2\omega}\left[\frac{e^2}{m^2\omega^2}\left(\mathbf{E}_1\cdot\nabla\right)\mathbf{E}_1 + \frac{ie^2}{m^2\omega c}\mathbf{E}_1\times\mathbf{B}_1\right]$$
$$+\frac{e}{i4\pi m\omega}\left(\nabla\cdot\mathbf{E}_1\right)\mathbf{E}_1 \qquad (9)$$

Neglecting for the moment the $(\nabla\cdot\mathbf{E})\mathbf{E}$ term, we may derive for the nonlinear polarization

$$\mathbf{P}_{NL} = \alpha\left(\mathbf{E}_1 \times \mathbf{B}_1\right) + \beta\mathbf{E}_1\left(\nabla\cdot\mathbf{E}_1\right) \qquad (10)$$

with

$$\alpha = \frac{i\rho^{(0)}e^2}{4\omega^3 m^2} \qquad \beta = \frac{\varepsilon e}{2m\omega^2}$$

The term with α is sometimes referred as the **"magnetic dipole"** and the one with β as **"electric quadrupole"** source.

Both terms are always polarized in the incidence plane (TM mode).

The first term is always present and is directed along $\vec{k}$

The second term arises only if the fundamental wave is polarized in the incidence plane.

Including the $(\nabla\cdot\mathbf{E})\mathbf{E}$ term of (9), which can be transformed as:

$$\mathbf{J}^{(2)}(2\omega)=\frac{i\rho^{(0)}}{2\omega}\left[\frac{e^2}{m^2\omega^2}(\mathbf{E}_1\cdot\nabla)\mathbf{E}_1+\frac{ie^2}{m^2\omega c}\mathbf{E}_1\times\mathbf{B}_1\right]+\frac{e}{i4\pi m\omega}(\nabla\cdot\mathbf{E}_1)\mathbf{E}_1 \qquad (9)$$

$$\begin{aligned}\frac{e}{i4\pi m\omega}(\nabla\cdot\mathbf{E})\mathbf{E}&=-\frac{e}{m\omega^2}\left[\nabla\cdot\left(\rho^{(0)}\mathbf{v}^{(1)}\right)\right]\mathbf{E}\\&=\frac{ie^2}{m^2\omega^3}\left[\nabla\cdot\left(\rho^{(0)}\mathbf{E}\right)\right]\mathbf{E}\\&=\frac{ie^2}{m^2\omega^3}\left[\frac{\nabla\rho^{(0)}\cdot\mathbf{E}}{1-\omega_p^2/\omega^2}\right]\mathbf{E}\end{aligned} \qquad (11)$$

where $\omega_p=\left(4\pi\rho^{(0)}e/m\right)^{1/2}$ is the plasma resonance frequency. With (11), $\mathbf{B}=(c/i\omega)\nabla\times\mathbf{E}$, and the vector relation $\mathbf{E}\times(\nabla\times\mathbf{E})+(\mathbf{E}\cdot\nabla)\mathbf{E}=\frac{1}{2}\nabla(\mathbf{E}\cdot\mathbf{E})$, the current density in (9) can be written as

$$\begin{aligned}\mathbf{J}^{(2)}(2\omega)&=\frac{i\rho^{(0)}e^2}{4m^2\omega^3}\nabla(\mathbf{E}\cdot\mathbf{E})+\frac{ie^2}{m^2\omega^3}\left[\nabla\cdot\left(\rho^{(0)}\mathbf{E}\right)\right]\mathbf{E}\\&=\frac{i\rho^{(0)}e^2}{4m^2\omega^3}\nabla(\mathbf{E}\cdot\mathbf{E})+\frac{ie^2}{m^2\omega^3}\left[\frac{\nabla\rho^{(0)}\cdot\mathbf{E}}{1-\omega_p^2/\omega^2}\right]\mathbf{E}\end{aligned} \qquad (12)$$

$$\mathbf{J}^{(2)}(2\omega) = \frac{i\rho^{(0)}}{2\omega}\left[\frac{e^2}{m^2\omega^2}(\mathbf{E}_1\cdot\nabla)\mathbf{E}_1 + \frac{ie^2}{m^2\omega c}\mathbf{E}_1\times\mathbf{B}_1\right]$$
$$+\frac{e}{i4\pi m\omega}(\nabla\cdot\mathbf{E}_1)\mathbf{E}_1 \qquad (9)$$

Eq.(9) shows explicitly that aside from the Lorentz term, there are also terms related to the spatial variation of E. They arise from the nonuniformity of the plasma. In a uniform plasma, $\nabla\rho^{(0)} = 0$ and $\nabla \cdot \mathbf{E} = 0$ from (11). This means that k is perpendicular to E and therefore $(E \cdot \nabla)E$ also vanishes. The Lorentz term is the only term in $J^{(2)}(2\omega)$

Coming back to (9), we may now write

$$\mathbf{P}_{NL} = \gamma \nabla \left(\mathbf{E}_1 \cdot \mathbf{E}_1 \right) + \beta \mathbf{E}_1 \left(\nabla \cdot \mathbf{E}_1 \right) \qquad (13)$$

instead of (10) where

$$\gamma = \frac{e^2 \rho_0}{8 m^2 \omega^4} \ .$$

In the bulk the electric field is divergenceless and only the first term in (13) contributes: near the surface both terms are important.

Adler for the first time speaks, for the centrosymmetric media, of two source terms for SH, one due to the magnetic dipole, due to the Lorentz force, and one due to the electric quadrupole, through the Coulomb force.

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Nonlinear Optical Frequency Polarization in a Dielectric

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(Received 25 July 1963)

A perturbation calculation of optical frequency polarization quadratic in the Maxwell field is made for a dielectric in which the electrons are localized on units of the crystal. The result is expressed in a power series in $K\langle r\rangle \sim 10^{-3}$ where $\langle r\rangle$ is the size of the unit and K is the wave number of the field. The term of zeroth order is the electric-dipole term which vanishes in a crystal with a center of symmetry. The term first order in $K\langle r\rangle$ is separated into electric-quadrupole and magnetic-dipole contributions by introducing a special gauge for the electromagnetic potentials. Higher power terms are neglected.

Jha used the model of the free electron gas in order to explain the SH in the metals and for first he wrote the second order polarization with the two terms, that represent the contribution of bulk and surface.

PHYSICAL REVIEW VOLUME 140, NUMBER 6A 13 DECEMBER 1965

Theory of Optical Harmonic Generation at a Metal Surface*†

SUDHANSHU S. JHA‡
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(Received 17 June 1965)

It is shown that a light wave of the high intensity obtainable from lasers produces a sufficiently strong nonlinear polarization on a reflecting metal surface to result in an observable amount of second harmonic generation. The analysis is based upon a self-consistent set of Maxwell's equations and the classical Boltzmann equation, respectively, for the electromagnetic fields and the distribution function of the conduction electrons. The conduction electrons are considered to be completely free except for a potential barrier at the metal surface, and the equations are solved for the fields varying with the frequency ω of the incident wave, and also for the fields varying with the frequency 2ω in the approximation where the surface barrier can be taken as a step potential. The effect of the incident light wave is treated as a perturbation to the motion of the electrons and the frequency ω is assumed to be less than half the plasma frequency ω_p so that neither the fundamental nor the second harmonic wave can lead to plasma resonance. The part of the polarization varying as $e^{-2i\omega t}$ which is quadratic in the incident field is found to have the form

$$\mathbf{P}_2(\mathrm{NL})=\alpha(\mathbf{E}_1\times\mathbf{H}_1)+\beta\mathbf{E}_1\mathrm{div}\mathbf{E}_1,$$

We look first at the component of $\mathbf{P}_{NL}$ parallel to the surface, $\mathbf{P}_{NL}^{\parallel}$; since $\mathbf{E}_1^{\parallel}$ is continuous across the surface, using translational symmetry in the plane of the surface we find

$$\mathbf{P}_{NL}^{\parallel} \simeq \beta \mathbf{E}_1^{\parallel} \left(\partial \mathrm{E}_1^{z} / \partial z \right), \qquad (14)$$

which gives a Dirac delta function at the surface in the limit of a step function equilibrium density profile. Thus there is an effective current sheet radiating at 2ω at the surface, and following back the derivation of eq.(14) it is clear that $\mathbf{P}_{NL}^{\parallel}$ results from the accumulated charge at the surface, signaled by the rapid variation in $\mathbf{E}_1^{z}$, being driven by the component of the electric field parallel to the surface. The magnitude of the current sheet due to $\mathbf{P}_{NL}^{\parallel}$ may be calculated in the free electron theory, since eq.(13) may be integrated across the surface.

For the normal component of $\mathbf{P}_{NL}$ the situation is different. From eq.(13) we find

$$\mathbf{P}_{NL}^{z} = \gamma \frac{\partial}{\partial z}\left[\left(\mathbf{E}_1^{z}\right)^2\right] + \beta \mathbf{E}_1^{z} \frac{\partial \mathbf{E}_1^{z}}{\partial z}, \qquad (15)$$

which is ambiguous, since both γ and $\mathbf{E}_1^{z}$ change discontinuously across the surface. Obviously, $\mathbf{P}_{NL}^{z}$, which appears in part because of the rapid variation of the normal field and in part because the response of electrons near the surface need not display inversion symmetry (1), is more subtle in nature than $\mathbf{P}_{NL}^{||}$. We note that even if the integral of eq.(15) could be performed, it is not clear whether the current sheet should be placed just inside or just outside the surface. This point is an ambiguity in the free electron model.

(1) J.Rudnick and E.A.Stern, PR B4 (1971) 4274

We conclude that the free electron theory only leads to physically meaningful results for the first order fields if a step function profile is adopted for the equilibrium electron density; in that limit, however, well-defined predictions for the second harmonic generation cannot be made. Of course, one would certainly expect the free electron theory to be less than accurate in the surface region where the actual fields vary over distances on the order of a few Fermi wavelengths; the point we wish to stress here is that the theory is in a sense somewhat worse: it is inherently ambiguous.

$\mathbf{P}_{NL}^{z}$

The term E x B originating from the Lorentz force acts on the current produced at the first order by B (it is nonlinear in B). It is a bulk current in the metal and does not irradiate except if there is a boundary.

The second term is a surface electric quadrupole term. It is present in nonlinear reflection from a metal and originates from the discontinuity of the normal component of E at the interface which generates nonlinear currents. The surface currents are a tangential component and a bulk one directed along z.

The SH polarization from the perpendicular and parallel surface currents can be written as

$$\mathbf{P}_z^{surface}(2\omega) \propto a(\omega)\mathbf{E}_z(\omega)\mathbf{E}_z(\omega)$$

and

$$\mathbf{P}_x^{surface}(2\omega) \propto b(\omega)\mathbf{E}_x(\omega)\mathbf{E}_z(\omega)$$

Rudnick and Stern argued from physical grounds that the second harmonic current sheet should be placed outside the bulk metal, and that its magnitude should be specified in terms of parameters *a* and *b* of order unity.

These conclusions are borne out to some extent by the application of the hydrodynamic theory of the electron gas to the calculation of SHG. The sheet is called selvedge (Sipe, Surf. Sci. 84, p. 75, 1979) and is smaller than λ. It is to be placed outside the bulk metal.

The free electron theory does not place unambiguously the current sheet.

J.Rudnick and E.A.Stern, PR B4 (1971) 4274

The coefficients a and b

Sipe et. al. gave an explicit expression for the parameters a and b with a free-electron hydrodynamic model and introduced an effective plasma frequency.

JJ.E.Sipe et al. Phys.Rev.B21(1980)4389

Using quantum theory, Weber and Liebsch (Phys. Rev. B36, 6411, 1987) showed that the sharp cutoff of the charge density at the surface introduces serious errors in the calculation of the perpendicular nonlinear surface currents.

Their calculation predicted a 1-2 orders of magnitude larger surface SH polarization.

The early experiments by Quail and Simon (Phys. Rev. B31, 4900, 1985) on the Al/glass and Ag/glass interfaces gave quite low values for *a* of the order of 1, however, this has to be attributed to the reduced SHG at the metal/glass interface compared to the metal/vacuum interface.

On the other hand, by quantitative measurements of the SH light from an Al surface in ultrahigh vacuum (UHV) at a laser wavelength of λ = 1.064 μm, Murphy et al. found a strong enhancement of the SHG at large angles of incidence. They derived *a* = -36 -9i, in very good agreement with the theoretical prediction. Furthermore, these experiments proved that for larger incident angles the SHG is determined mainly by the perpendicular nonlinear surface current for the vacuum/metal interface.

R. Murphy, M. Yeganeh, K. Song, E. Plummer, Phys. Rev. Lett. 63, 318 (1989).

Despite the good agreement of theory and experiment on the second harmonic response normal to the surface, significant discrepancies are evident at smaller incident angles where signs of an anisotropic SH response are detected.

This anisotropy can only arise from interband transitions, i.e. from the periodic lattice potential, which had not been included in the theory.

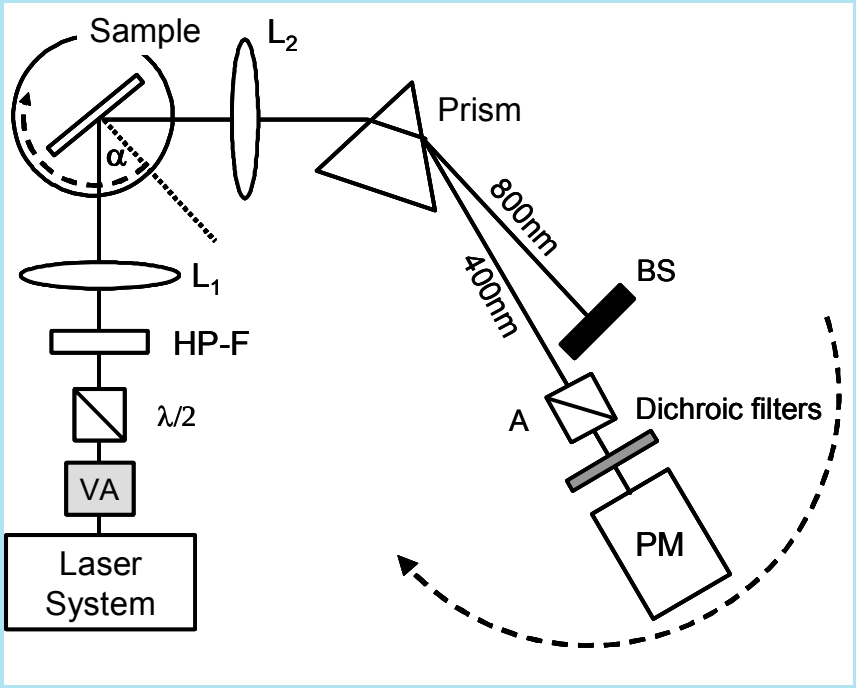
H. Tom, G. Aumiller, Phys. Rev. B33, 8818 (1986).
K. Pederson. O. Keller, J. Opt. Spectr. Am. B6, 2412 (1989).

Strong azimuthal anisotropy has been observed on a number of metal surfaces (see table).

Surface	Element	Reference
(111)	Al	R. Murphy, M. Yeganeh, K. Song, E. Plummer, Phys. Rev. Lett. 63, 318 (1989)
		S. Janz, K. Pedersen, H. van Driel, Phys. Rev. B44, 3943 (1991)
		Z. Ying, J. Wang, G. Andronica, J. Yao, E. Plummer, J. Vac. Sci. Technol. A11, 2255 (1993)
	Cu	H. Tom, G. Aumiller, Phys. Rev. B33, 8818 (1986)
		J. Bloch, G. Lubke, S. Janz, H. van Driel, Phys. Rev. B45, 12011 (1992)
	Ni	R. Anderson, J. Hamilton, Phys. Rev. B38, 8451 (1988)
	Ag	R. Bradley, R. Georgiadis, S. Kevan, G. Richmond, J. Vac. Sci. Technol. A10, 2996 (1992)
		C. Li, L. Urbach, H. Dai, Phys. Rev. B49, 2104 (1994)
		E. Wong, G. Richmond, J. Chem. Phys. 99, 5500 (1993)
		E. Wong, K. Friedrich, G. Richmond, Chem. Phys. Lett. 195, 628 (1992)
		R. Georgiadis, G. Richmond, J. Chem. Phys. 95, 2895 (1991)
	Au	E. Wong, G. Richmond, J. Chem. Phys. 99, 5500 (1993)
		A. Friedrich, C. Shannon, B. Pettinger, Surf. Sci. 251/252, 587 (1991)
		V. Daniel, A. Koos, G. Richmond, J. Phys. Chem. 94, 2091 (1990)
		D. Koos, G. Richmond, J. Phys. Chem. 96, 3770 (1992)
(110)	Cu	M. Hoffbauer, V. McVeigh, M. Zuerlein, J. Vac. Sci. Techol. B10, 268 (1992)
		J. Woll, G. Meister, U. Barjenbruch, A. Goldmann, Appl. Phys. A60, 173 (1995)
	Ag	V. Daniel, D. Koos, G. Richmond, J. Phys. Chem 94, 2091 (1990)
		D. Koss, V. Shannon, G. Richmond, Phys. Rev. B47, 4730 (1993)
		L. Urbach, K. Percival, J. Hicks, E. Plummer, H. Dai, Phys. Rev. B45, 3769 (1992)
		S. Reiff, J. Bloch, Surf. Sci. 345, 281 (1996)
	Au	G. Lupke, G. Marowsky, R. Steinhoff, A. Friedrich, B. Pettinger, D. Kolb, Phys. Rev B41, 6913 (1990)
(001)	Al	K. Pederson, O. Keller, J. Opt. Spectr. Am. B6, 2412 (1989)
		D. Koss, V. Shannon, G. Richmond, Phys. Rev. B47, 4730 (1993)
	Cu	D. Koss, V. Shannon, G. Richmond, Phys. Rev. B47, 4730 (1993)
		R. Vollmer, M. Straub, J. Kirschner, Surf. Sci. 352-354, 684 (1996)
	Ag	D. Koss, V. Shannon, G. Richmond, Phys. Rev. B47, 4730 (1993)
	Au	D. Koss, V. Shannon, G. Richmond, Phys. Rev. B47, 4730 (1993)

Dependence on fundamental beam polarization direction

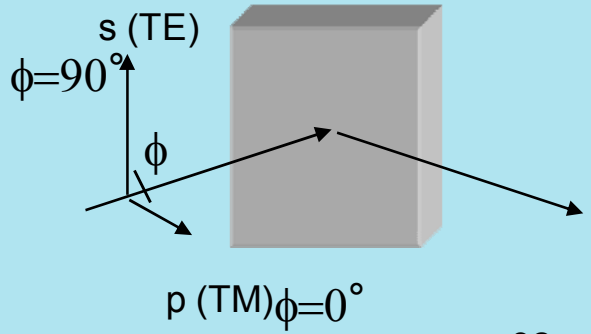
- A typical apparatus is shown in the figure
- Since the surface nonlinear sources are in the simplest theory proportional to $(\nabla\cdot\mathbf{E})\mathbf{E}$, then incident fields polarized only in the plane of the surface (normal to the plane of incidence) do not contribute to the second harmonic signal.
- However the bulk terms proportional to $\mathbf{E}\times\mathbf{H}$ lead to harmonic generation for all incidence polarizations



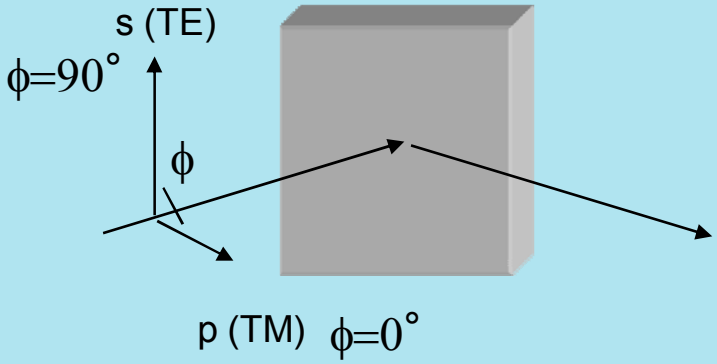
Dependence on fundamental beam polarization direction

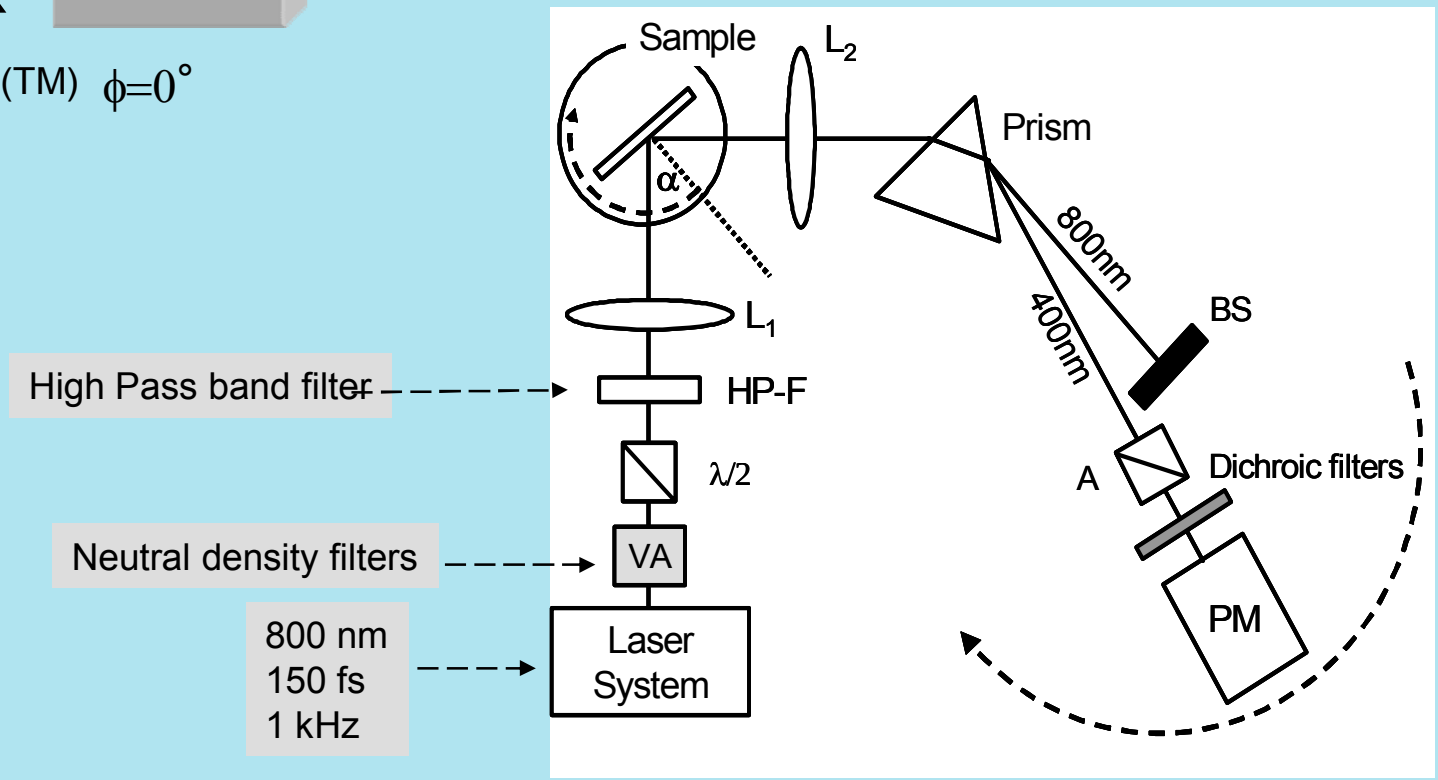
- **Neglecting bulk terms, a [cos(ϕ)]^4 dependence on the polarization is predicted, where ϕ is the electric field angle relative to the plane of incidence.**
- **Deviations from this relation are indicative of contributions from the bulk term, and in particular the ratio**
- **$M = I^{SH}(\phi=90^\circ) / I^{SH}(\phi=0^\circ)$**
- **yields information about the relative strengths of the surface versus bulk terms**

- **F.Brown et al., PRL 14 (1965) 1029**
- **F.Brown and R.E.Parks, PRL 16 (1966) 507**
- **N. Bloembergen et al., PR 174 (1968) 813**



Experimental Setup





First experimental results

VOLUME 14, NUMBER 25 PHYSICAL REVIEW LETTERS 21 JUNE 1965

NONLINEAR OPTICAL REFLECTION FROM A METALLIC BOUNDARY*

Fielding Brown, Robert E. Parks, and Arthur M. Sleeper

Williams College, Williamstown, Massachusetts

(Received 3 May 1965)

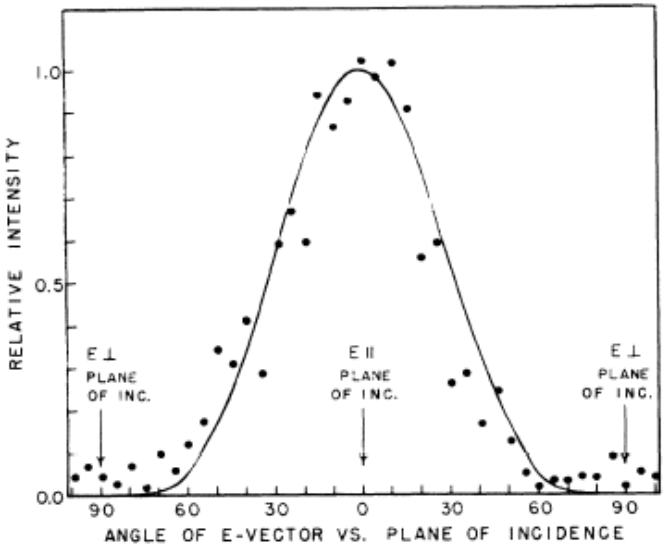


FIG. 2. Variation of second-harmonic light intensity with angle θ between the incident-light polarization vector and the plane of incidence. The theoretical $\cos^4\theta$ dependence (solid line) is included for comparison.

Summary of second harmonic production in metals

The first theoretical prediction of the SHG of light from a free-electron gas was presented by Jha (1) in 1965. Later, the first conclusive experimental observation of the SHG from a silver film excited by a ruby laser light was reported by Brown et al.(2,3). Research in SHG from metal surfaces has been expedited by discoveries of the enhanced scattered SHG from roughened silver surfaces (4), from molecular monolayers absorbed on a silver surface (5,6), and from nonlinear surface-plasmon effects (7-9). Exploiting SHG from the surface of centrosymmetric media as a new probe for studies of surface physics has been demonstrated by several authors (10).

(1) J.Jha, Phys. Rev. 140, A2020 (1965).

(2) F. Brown, R.E. Parks, A.M. Sleeper, Phys. Rev. Let. 14, 1029 (1965).

(3) F. Brown, R.E. Parks, Phys. Rev. Lett. 16, 507 (1966).

(4) C.K. Chen, T.F. Heinz, D. Ricard, Y. Shen, Phys. Rev. Lett. 46, 145 (1981).

(5) C.K. Chen, T. Heinz, D. Ricard, Y. Shen, Phys. Rev. Lett. 46, 1010 (1981).

(6) G. Boyd, Y. Shen, Opt. Lett 11, 97 (1986).

(7) H. Simon, D. Mitchell, J. Watson, Phys. Rev. Lett. 33, 1531 (1974).

(8) J. Quail, J. Rako, H. Simon, R. Deck, Phys. Rev. Lett. 50, 1987 (1983).

(9) J. Quail, H. Simon, J. Appl. Phys. 56, 2589 (1984).

(10) H. Tom, C. Mate, X. Zhu, J. Crowell, T. Heinz, G. Somorjai, Y. Shen, Phys. Rev. Lett. 52, 348 (1984).

An excellent review of SHG from metal surfaces is by Sipe & Stegeman (1).

The sources of SHG on a metal surface consist of a "**volume**" current density which extends over skin depth and a "**surface**" current density penetrating only a few Fermi wavelengths into a metal (the so-called selvedge region).

The free-electron model is inadequate to describe the electron dynamics in the selvedge region. Rudnick and Stern (2) first pointed out the limitations of the free-electron model in describing the SHG surface-current sources and proposed two phenomenological parameters *a* and *b* to estimate the size of these current sources.

(1) J. Sipe, G. Stegeman, in Surface Polaritons: Electromagnetic Waves at Surfaces and Interfaces, ed. by V. Agranovich and D. Mills (North-Holland, Amsterdam, 1982), p.661.

(2) J. Rudnick, E. Stern, Phys. Rev. B4, 4274 (1971).

Sipe et. al (1) have given an explicit expression for these parameters with a free-electron hydrodynamic model and have introduced an effective plasma frequency. They have done calculations with b = -1 for a smooth metal surface, allowing the parameter a to be determined by experiments. This theory along with the experimental results for the SHG in a total-internal-reflection (TIR) geometry from a prism-metal interface over a broad range of incident angles can successfully determine the parameter a of noble metals and aluminium films (2,3).

(1) J. Sipe, V. so, M. Fukui, G. Stegeman, Phys. Rev. B21, 4389 (1980).

(2) J. Quail, H. Simon, Phys. Rev. B31, 4900 (1985).

(3) C. Tzeng, J. Lue, Surf. Sci. 192, 491 (1987).

In 1969 , observation of a strong dependence of SHG signal at silver surfaces on the amount of absorbed silver was the first indication of the surface sensitivity of SHG [1].

Rudnick and Stern [2] realized that the surface sensitivity of SHG was primarily attributed to the broken inversion symmetry of the surface rather than the quadrupolar effects.

(1) F.Brown and M.Matsuoka, Phys.Rev. 185(1965)985
(2) J.Rudnick and E.A.Sterns, Phys.Rev. B4(1971)4274

Guyot-Sionnest et al. [1] estimated that the contribution from the bulk nonlinearity to SHG was an order of magnitude weaker than the surface nonlinearity in centrosymmetric media with large optical dielectric constant such as metals and semiconductors.

(1) P.Guyot-Sionnest et al.,hys.Rev. B33(1986)8254

Composite materials

- It is possible to combine two or more optical materials in such a manner that the effective nonlinear optical susceptibility of the composite material exceeds those of its constituents.
- Some structure is shown in the figure. In each case, the characteristic distance scale over which the constituent materials are mixed is much smaller than an optical wavelength.
- Consequently, the propagation of a beam of ligth through such material can be described by spatially averaged values of the linear and nonlinear refractive indices obtained by performing suitable volume averages.

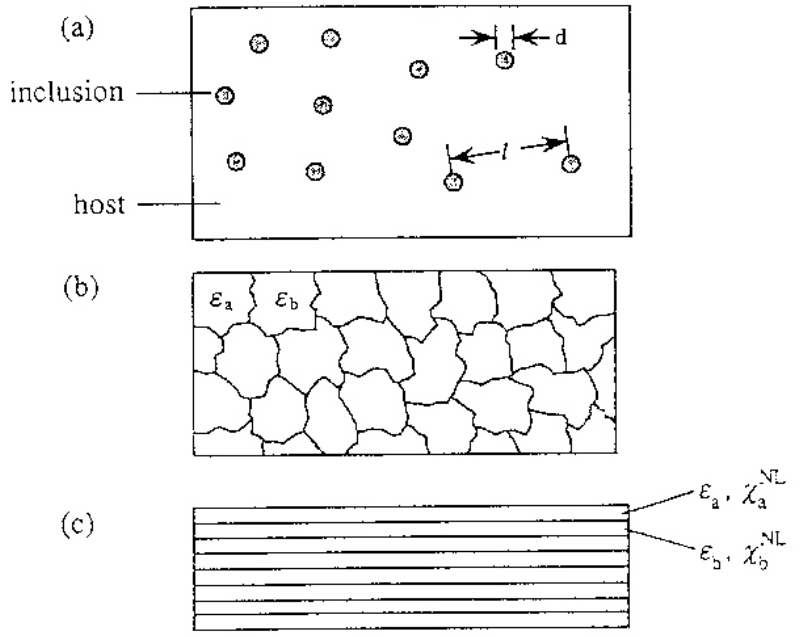


Figure 1. Several of the structures that have been considered for the development of composite nonlinear optical materials. (a) The Maxwell Garnett geometry; (b) the Bruggeman or interdispersed geometry, and (c) the layered geometry.

- J.E. Sipe and R.W.Boyd, PR A46 (1992) 1614; JOSA B11 (1994) 297
- G.L.Fischer et al. PRL 74 (1995) 1871

Structures

- **If the two constituent materials of the composite posses different linear refractive indices, the electric field of the incident laser beam will become spatially nonuniform within the material. Under proper conditions, the electric field amplitude will become concentrated in the more nonlinear constituent of the composite, resulting in an enhanced overall nonlinear optical response.**

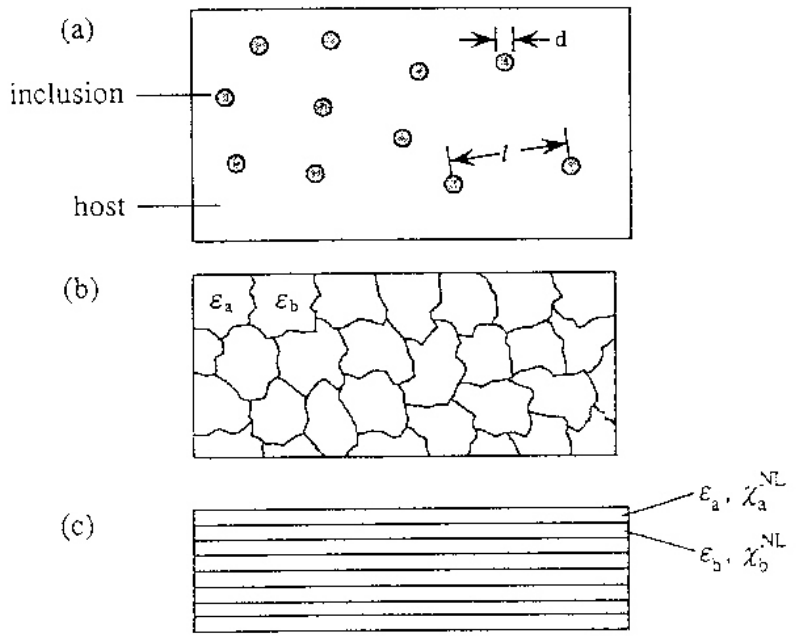


Figure 1. Several of the structures that have been considered for the development of composite nonlinear optical materials. (a) The Maxwell Garnett geometry; (b) the Bruggeman or interdispersed geometry, and (c) the layered geometry.

- Much of the early work on composite nonlinear optical materials concerned metallic colloids.

- For such materials, an enhancement of the electric field occurs in the vicinity of each metallic particle.

- The enhancement is particularly large when the laser frequency is near that of the surface plasmon resonance of the metallic particle

- D.Ricard et al. Opt. Lett. 10 (1985) 511
- F.Hache et al. Appl. Phys. A47 (1988) 347

Spherical particles a << λ dispersed with a very low volume fraction f << 1.

A single spherical inclusion experiences a local field E_{loc}

$$\vec{E}_{loc} = \vec{E} + \frac{4\pi\vec{P}}{3\varepsilon_h} \qquad (28)$$

and the field inside it is

$$\vec{E}_i = \frac{3\varepsilon_h}{\varepsilon_i + 2\varepsilon_n} E_{loc} \qquad (29)$$

If the inclusion is made of a metal with

$$\mathrm{Re}(\varepsilon_i) < 0$$

one may choose the host and the inclusion dielectric constant such that

$$\mathrm{Re}(\varepsilon_i + 2\varepsilon_h) = 0$$

corresponding to the plasmon resonances, thus obtaining resonant enhancement effects. Thus the inclusion can experience an enhanced local field that, in case of several inclusions randomly dispersed in the host, leads to an effective dielectric constant ε_{eff} that satisfies

$$\frac{\varepsilon_{eff} - \varepsilon_h}{\varepsilon_{eff} + 2\varepsilon_h} = \beta f \quad with \quad \beta = \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h} \qquad (30)$$

where f is the volume fraction of the inclusion material.

Here we consider the optical Kerr effect of randomly interdispersed composite materials which, for monochromatic beams, is represented by a third-order polarization $P^{(3)}$ at frequency ω induced by an electric field E at the same frequency,

$$P^{(3)}(\omega) = 3\chi^{(3)}\left(\omega, -\omega, \omega\right)\left|E(\omega)\right|^2 E(\omega) \qquad (38)$$

It may be described by an optically induced change of the optical dielectric constant

$$\delta\bar{\varepsilon} = 12\pi\bar{\chi}^{(3)}\left|E(\omega)\right|^2. \qquad (39)$$

For metal inclusions in the limit $f << 1$, so that each metal nanoparticle is entirely surrounded by the host dielectric medium and the interparticle spacing is large with respect to the size of the nanoparticles and much smaller than λ, Flytzanis *et al* [1,2,3], assuming that the inclusion material has a nonlinear susceptibility $\chi^{(3)}$, gave an expression for the change in the inclusion dielectric constant

$$\delta\varepsilon_{eff} = f\left(\frac{3\varepsilon_h}{\varepsilon_i + 2\varepsilon_h}\right)^2 \left|\frac{3\varepsilon_h}{\varepsilon_i + 2\varepsilon_h}\right|^2 12\pi\chi^3 |E|^2$$

$$= fx^2 |x|^2 12\pi\chi^{(3)} |E|^2 \qquad (40)$$

[1] C. Flytzanis, F. Hache, C. Klein, D. Ricard, P. Roussignol, Prog. Opt. XXIX, 321 (1991)
[2] K. Roustagi, C. Flytzanis, Opt. Lett. 9, 344 (1984)
[3] D. Ricard, P. Roussignol, C. Flytzanis, Opt. Lett. 12, 511 (1985)

where

$$x = \frac{3\varepsilon_h}{\varepsilon_i + 2\varepsilon_h} \qquad (41)$$

or

$$\bar{\chi}^{(3)}_{eff} = p\left|f_1\right|^2 f_1^2 \chi^{(3)}_m \qquad (42)$$

where

$$f_1(\omega) = \frac{3\varepsilon_d}{\varepsilon_m(\omega) + 2\varepsilon_d} \qquad (43)$$

ε_m and ε_d being the dielectric constant of the metal particles and the surrounding dielectric respectively and $\chi^{(3)}_m$ the third-order nonlinear susceptibility of the metal particle itself. $\chi^{(3)}_m$ can be separated into three contributions [1]:

$$\chi_m^{(3)} = \chi_{intra}^{(3)} + \chi_{inter}^{(3)} + \chi_{va}^{(3)}$$

[1] F. Hache, D. Ricard, C. Flytzanis, J.O.S.A. B3 1647 (1986).

$$\chi_m^{(3)} = \chi_{intra}^{(3)} + \chi_{inter}^{(3)} + \chi_{re}^{(3)}. \qquad (45)$$

The first and second terms result from the familiar intraband and interband transitions.

The third contribution is due to the modification of the populations of the electrons resulting from the large increase in the electron temperature caused by resonant absorption of photons, but before thermalization. After the lattice is heated up there is an additional term $\chi_{thermal}^{(3)}$ which is a much slower process (ns or longer).

Values of $\chi_{eff}^{(3)}$ of the order of 5×10^{-8} esu have been measured in gold with $f \sim 10^{-5} - 10^{-6}$.

Measurements of $\chi_{eff}^{(3)}$ have been made by Liao[1] for increasing values of *f* and are shown in the figure. The susceptibility increases linearly with *f* up to about $f \simeq 0.15$, beyond which it increases much more quickly to decrease after $f = 0.28$ as the percolation threshold is approached. Mie scattering resonances are identified as the cause of this behaviour.

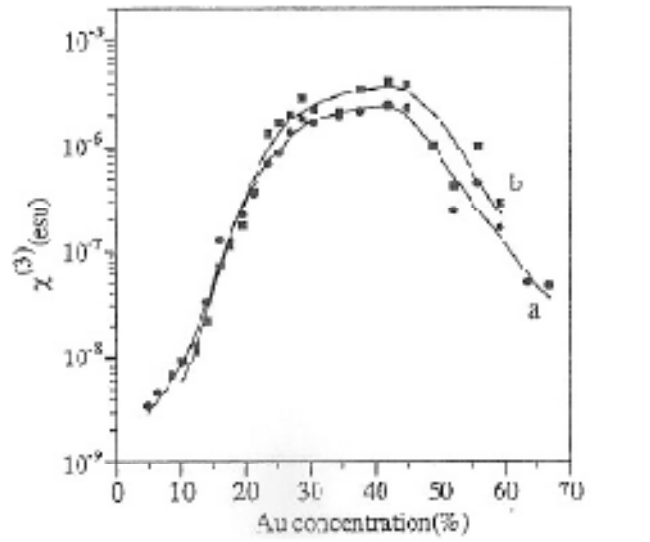


Figure 27. Concentration dependence of $\chi^{(3)}$ measured by forward degenerate four-wave mixing (a) and backward degenerate four-wave mixing (b). Both measurements yield essentially the same result. The data between $f = 0.15$ to 0.28 can be fitted reasonably well by a power law $\chi^{(3)} \sim f^3$

[1] H. B.Liao et al. Appl. Phys.Lett. 70(1997)1

Agarwal and Dutta Gupta [1], assuming Kerr-type nonlinearity in the inclusions, obtained an effective cubic susceptibility $\chi_{eff}^{(3)}$ given by

$$4\pi\chi_{\text{eff}}^{(3)} = f\frac{|x|^2 x_2}{|1+f(x-1)|^2(1+f(x-1))^2}\chi_2^{(3)}. \qquad (46)$$

Other alternative structures have been proposed, such as those obtained by alternating layers of two different materials [2,3]. In this case, a prediction of enhanced nonlinear response has been given for suitable polarization of light and it has been shown that metallic composites with fractal structures have large nonlinear susceptibilities [4–6]; such structures take advantage of their localization properties of the electromagnetic field [7].

[1] Agarwal G S and Gupta S D 1988 Phys. Rev. A 38 5678

[2] Boyd R W and Sipe J E 1992 Phys. Rev. A 46 1614

[3] Boyd R W and Sipe J E 1994 J. Opt. Soc. Am. B 11 297

[4] Butenko A V, Shalaev V M and Stockman M I 1988 Sov. Phys.—JETP 7 60

[5] Butenko A V, Chubarov P A, Danilova Y E, Karpov S V, Popov A K, Rautian S G, Safonov V P, Slabko V V, Shalaev V and Stockman M I 1990 Z. Phys. D 17 283

[6] Shalaev V 2002 Optical Properties of Nanostructured Random Media (Berlin: Springer)

[7] Bertolotti M, Masciulli P and Sibilia C 1994 Opt. Lett. 19 777

Boyd and Sipe considered layered composites comprising alternating layers of two or more constituents, with each layer having a width << λ. In the case of an electric field parallel to the surface, the effective nonlinear susceptibility is

$$\chi_{\text{eff}}^{\text{nl}} = f_1 \chi_1^{\text{nl}} + f_2 \chi_2^{\text{nl}} \qquad (47)$$

where χ_i^{nl} is the nonlinear susceptibility of the *i*th constituent.

The case of an electrical field polarized perpendicular to the layers is more interesting. The effective third-order nonlinearity $\chi_{eff}^{(3)}$ is given by

$$\chi_{\text{eff}}^{(3)}(\omega = \omega + \omega - \omega) = f_1 \left(\frac{\varepsilon_L(\omega)}{\varepsilon_1(\omega)}\right)^2 \left|\frac{\varepsilon_L(\omega)}{\varepsilon_1(\omega)}\right|^2 \chi_1^{(3)}$$
$$+ f_2 \left(\frac{\varepsilon_L(\omega)}{\varepsilon_2(\omega)}\right)^2 \left|\frac{\varepsilon_L(\omega)}{\varepsilon_2(\omega)}\right|^2 \chi_2^{(3)} \qquad (48)$$

where

$$\frac{1}{\varepsilon_L} = \frac{f_1}{\varepsilon_1} + \frac{f_2}{\varepsilon_2} \qquad (49)$$

Conclusions

Considering metallic inclusions, non linearities are effective on a nanometric scale and may be strongly enhanced by plasmon resonances.

Nonlinearities can be controlled in nanostrustured materials.