[5]J. M. J. Van Leeuwen and A. Weijland, Phys. Letters 19, 562 (1965).
[6]S. F. Edwards, Phil. Mag. 3, 33, 1020 (1958).
[7]J. S. Langer, Phys. Rev. 120, 714 (1960); see also J. S. Langer, Phys. Rev. 124, 1003 (1961), for a more complete analysis of the many-body aspects of this problem.
[8]M. L. Glasser, Phys. Rev. 129, 472 (1963).

SECOND-HARMONIC GENERATION OF LIGHT IN REFLECTION FROM MEDIA WITH INVERSION SYMMETRY

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The second-harmonic generation (SHG) of light in reflection[1] has been extensively studied in crystals lacking a center of inversion.[2] In media with inversion symmetry, the second-harmonic source terms are smaller in magnitude and have magnetic-dipole and/or electric-quadrupole character.[3] Recently, reflected second-harmonic light from metallic silver[4] and from silicon and germanium[5] has been reported. Some discussion has arisen whether the effect in silver is due mostly to the free-electron plasma[6-8] or whether core electrons contribute significantly to the observed second-harmonic intensity.[5,9,10] It is the purpose of this note to present new theoretical and experimental evidence that the latter viewpoint is correct.

In general one may expect that, if both conduction electrons and core electrons make comparable contributions to the linear dielectric constant, they will also make comparable contributions to the nonlinear susceptibilities.[11] It is well known that the linear dielectric constant in silver at the second-harmonic frequency of ruby-laser light contains about equal and opposite contributions from the intraband (conduction electron) and interband (core) transitions.[12] A general formula for the nonlinear source current density incorporates both contributions.[13] An expansion into multipole moment contributions has been made.[3,14]

For an isotropic medium[15] the important source terms at the second-harmonic frequency may be written in the pheonomenological form

$$\vec{P}^{NL}(2\omega)=\alpha(\vec{E}\times\vec{H})\equiv(\alpha_{pl}+\alpha_c)(\vec{E}\times\vec{H}), \quad (1)$$

$$-\nabla\cdot Q^{NL}(2\omega)=-\nabla\cdot(\beta_{pl}'+\beta_c')\vec{E}\vec{E}. \quad (2a)$$

The divergence of the volume quadrupolarization may be transformed into a surface term of the form used by Jha,[7]

$$\vec{P}_{eff}^{NL}=+(\beta_{pl}+\beta_c)\vec{E}(\nabla\cdot\vec{E}), \quad (2b)$$

with

$$\beta_{pl}+\beta_c=-(\beta_{pl}'+\beta_c')/(\epsilon_{(\omega)}-1).$$

All values of the fields should be taken inside the medium. They are related to the incident laser field by the linear Fresnel equations. The magnitude of the quadrupole volume term is equivalent to that of a dipole term restricted to a single atomic layer at the surface.

It must be emphasized that these phenomenological relationships hold equally well for free as for bound electrons. Any attempt to decide on the basis of polarization properties alone that a pure plasma effect is involved has no validity. The symmetry properties of the core electrons are the same as for the conduction electrons. We have indeed found that the polarization properties, the variation with angle of incidence, as well as the magnitude of the reflected harmonic intensity from Si and Ge are very similar to those from Ag, Au, Cu, and other metals.

The suggestion that the laser beam first creates a plasma in Si and Ge in our experiments has been disproved as follows. The reflectivity of the Si and Ge samples was monitored with a continuous beam at 6328 Å from a He-Ne laser. No observable change in reflectivity occurred during the ruby-laser pulse which created the second harmonic. The induced plasma density is negligible at the power levels used in our experiment. Furthermore, the SHG was found to be strictly proportional to the square of the laser intensity. If a plasma must first be created, the SHG would be proportional to a higher power.

When the source terms (1) and (2b) are substituted, respectively, into Eqs. (4.12) and (6.22) of Ref. 1, the following ratio for intensity of the second-harmonic intensity to the incident intensity, polarized in the plane of incidence, results as a function of the angle of incidence θ:

$$R=\left(\frac{eE_{\text{inc}}}{m\omega_p c}\right)^2 \sin^2\theta\cos^4\theta\left(\frac{\omega_p}{\omega}\right)^6 \times\frac{|\epsilon(\omega)(1+\alpha_{\text{core}}/\alpha_{pl})+4(1+\beta_{\text{core}}/\beta_{pl})[\epsilon(\omega)-\sin^2\theta]^{1/2}[\epsilon(2\omega)-\sin^2\theta]^{1/2}|^2}{|\epsilon(2\omega)\cos\theta+[\epsilon(2\omega)-\sin^2\theta]^{1/2}|^2|\epsilon(\omega)\cos\theta+[\epsilon(\omega)-\sin^2\theta]^{1/2}|^4}, \tag{3}$$

where the plasma frequency is given by $\omega_p^2 = 4\pi ne^2/m$. The notation has been chosen so as to correspond most closely to that adopted by Jha.[6,7] The complex dielectric constant $\epsilon(\omega)$ contains both plasma and core contributions. If one puts $\alpha_{\text{core}}=\beta_{\text{core}}=0$, and $\epsilon(\omega)=1-(\omega_p^2/\omega^2)$, Eq. (3) reduces to the bare-plasma case discussed by Jha. There are corresponding expressions for the case that the incident polarization has a component perpendicular to the plane of incidence.

We have measured the ratio M of second-harmonic intensity for polarization of the incident laser perpendicular and parallel to the plane of incidence. The results are given in Table I. The last column gives the values used by Brown and Jha for the bare plasma. The next to last column gives the values to be expected when the core nonlinearity is ignored, but the core contribution to the linear dielectric constant is taken into account. Agreement with the observed values is only obtained if the nonlinear core contribution is included. Note that the value for Ag is found to be frequency sensitive. At 6943 Å the values for Ag are accidentally such that $\alpha_c/\beta_c=\alpha_{pl}/\beta_{pl}$, so that the same ratio is obtained with or without core nonlinearity. This is not so in the other cases. The dependence on the angle of incidence θ, as given by Eq. (3), has been checked both for Ag and for Si.

Table I. The ratio of the second-harmonic reflected intensity, when the incident laser beam is polarized parallel and perpendicular to the plane of incidence.

	Fundamental wavelength Å	M, experimental	M, core linear	M, plasma only
Ag	6943	0.066 ± 0.013	0.068	0.031
Ag	8658	0.066 ± 0.013	0.042	0.030
Au	6943	0.083 ± 0.016	0.038	0.030
Ge	6943	0.11 ± 0.020	⋯	⋯

A more definite test about the core nonlinearities is obtained by measuring the second-harmonic intensity as a function of frequency. The observed absolute value for this intensity is obtained by calibration with the harmonic intensity from a GaAs mirror. The experimental points, shown in Fig. 1, deviate considerably from the drawn curves which are calculated from Eq. (3) with $\alpha_{\text{core}}=\beta_{\text{core}}=0$. Apparently the core nonlinearity interferes destructively with the plasma contribution.

Note that the interband contribution to the linear dielectric constant also has the opposite sign from that due to the plasma. The nonlinear core contribution in Ag becomes important at about $2\hbar\omega_L = 3$ eV, in agreement with the fact that the core contribution is important in the linear dielectric at about this energy. The nonlinear core contribution in Ag tends to obliterate the effect of the resonance in the linear dielectric constant, $\epsilon(2\omega) = 0$, which by itself gives rise to the pronounced maximum in the drawn curve for the case $\alpha_{\text{core}} = \beta_{\text{core}} = 0$.

This interpretation is confirmed by the data of second-harmonic production in Ag-Au alloys, shown in Fig. 2. The alloys were made by simultaneous controlled evaporation of Ag and Au, and the layers were analyzed by nondestructive quantitative electron-probe microanalysis. It is known from linear optical data that the addition of a few percent Au to Ag shifts the resonance, $\epsilon'(2\omega)=0$, to lower frequencies. At the same time $\epsilon''(2\omega)$ increases and the reflectivity loses the pronounced minimum it has in pure Ag. The second-harmonic production nicely reproduces the variation of $\epsilon(2\omega)$ in Eq. (3) as up to 5% Au is added.

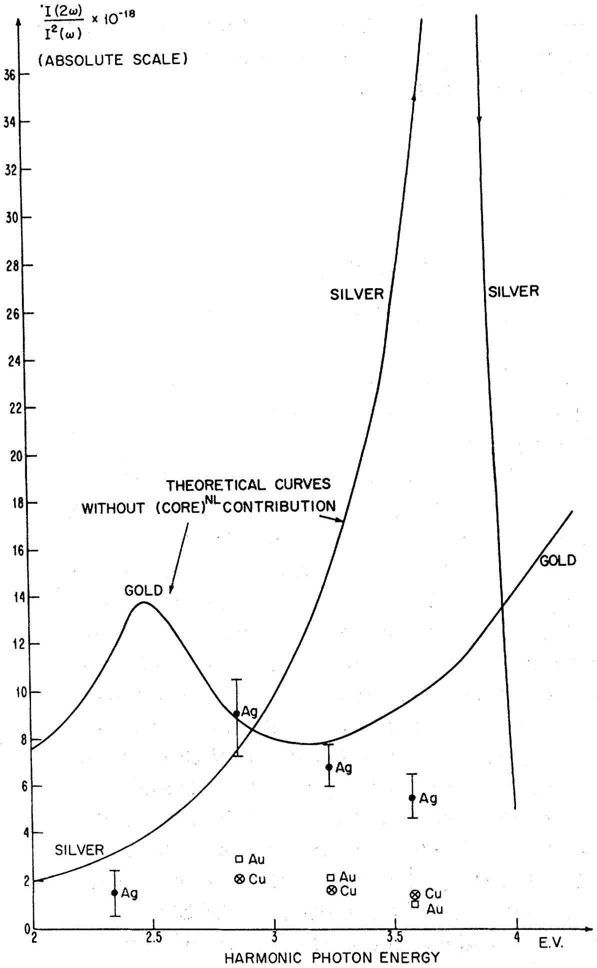

FIG. 1. The dispersion of the second-harmonic intensity, reflected from silver, gold, and copper. The drawn curve is computed in the absence of a core contribution to the nonlinearity. The angle of incidence is 45°.

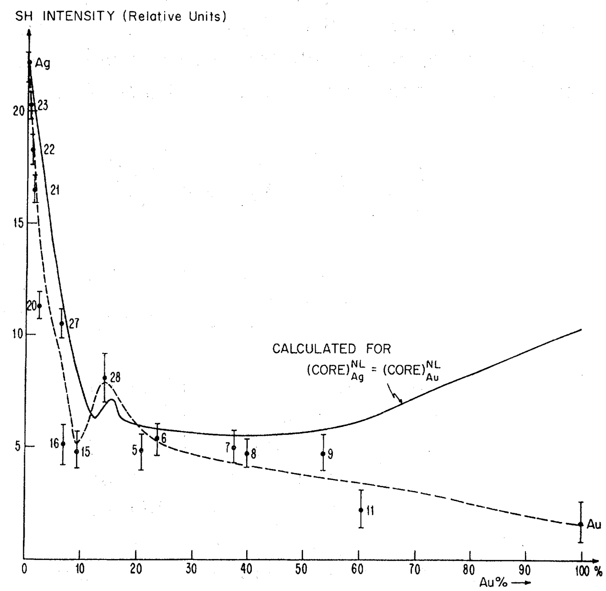

FIG. 2. The second-harmonic generation by a ruby laser reflected from Ag - Au alloys. The drawn curve is computed with a core nonlinearity corresponding to match the experimental point for pure silver. The angle of incidence is 45°.

The drawn curve is calculated from Eq. (3) with the known variation of ϵ as a function of composition,[16] while α_{core} and β_{core} are taken equal to the value for pure Ag. The important deviation from the experimental points toward the gold-rich side is caused by the fact that the core nonlinearity of Au atoms is substantially different from that of Ag atoms. The plasma contribution in pure Ag and pure Au is essentially the same.

These data prove conclusively that the core or interband contributions to the optical nonlinearity in metals are comparable to the plasma or intraband contributions, in agreement with general theoretical considerations. The symmetry and polarization properties for the effect in Si and Ge are the same as those for metals, although only interband transitions contribute in the case of these semiconductors. For these materials it has been possible to observe a change in the reflected harmonic intensity by the application of a strong dc electric field. This has been accomplished by immersing the sample in an electrolytic KCl solution with a small applied voltage.[17] The electric-field-induced harmonic polarization can interfere constructively or destructively with the source terms in Eqs. (1) and (2), depending on the sign of the applied voltage. A total enhancement of about a factor of 3 in the second-harmonic intensity generated from Ge has been achieved.

A detailed report on all these effects is in the course of preparation. The authors are indebted to Professor P. S. Pershan for discussions on the relationship between the volume quadrupole and the surface dipole effect. They also wish to thank Professor W. Paul for suggesting the field-induced polarization by electrolytic solutions. Helpful discussions with Professor H. Ehrenreich on the optical properties of metals are also acknowledged.

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[1]N. Bloembergen and P. S. Pershan, Phys. Rev. 128, 606 (1962).
[2]R. K. Chang and N. Bloembergen, Phys. Rev. 144, 775 (1966), and earlier references quoted therein.
[3]P. S. Pershan, Phys. Rev. 130, 919 (1963).
[4]F. Brown, R. E. Parks, and A. M. Sleeper, Phys. Rev. Letters 14, 1029 (1965).
[5]N. Bloembergen and R. K. Chang, in Physics of Quantum Electronics, edited by P. L. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill Book Company, Inc., New York, 1966), p. 80; N. Bloembergen and Y. R. Shen, ibid., p. 119.
[6]S. S. Jha, Phys. Rev. Letters 15, 412 (1965).
[7]S. S. Jha, Phys. Rev. 140, A2020 (1965).
[8]F. Brown and R. E. Parks, Phys. Rev. Letters 16, 507 (1966).
[9]N. Bloembergen and Y. R. Shen, Phys. Rev. 141, 298 (1966).
[10]R. K. Chang, N. Bloembergen, and C. H. Lee, Bull. Am. Phys. Soc. 11, 111 (1966).
[11]R. C. Miller, Appl. Phys. Letters 5, 17 (1964).
[12]H. Ehrenreich and H. R. Philipp, Phys. Rev. 128, 1622 (1962).
[13]H. Cheng and P. B. Miller, Phys. Rev. 134, A683 (1964).
[14]E. Adler, Phys. Rev. 134, A728 (1964).
[15]The evaporated metal samples are indeed isotropic on the scale of an optical wavelength. Single crystals of silicon and germanium may display additional terms, although the existing experimental data could not distinguish between cubic and isotropic symmetry. No dependence of the second-harmonic intensity on the crystallographic orientation of the surface plane could be detected. The harmonic magnetic dipole source vanishes for isotropic samples, $\vec{M}^{NL}(2\omega)=\gamma\vec{E}\times\vec{E}=0$.
[16]H. Fukutani and O. Sueoka, private communication.
[17]K. L. Shaklee, F. H. Pollak, and M. Cardona, Phys. Rev. Letters 15, 883 (1965).

PLASMA RESONANCE IN THE PHOTOELECTRIC YIELD OF ALUMINUM*

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Aluminum is known to behave like a free-electron gas in a wide range around its plasma frequency. A characteristic electron energy loss of 15 eV which is unambiguously due to the excitation of a plasmon has been reported by many authors.[1] The radiative decay of the plasmon into a photon, the so-called plasma radiation,[2] has also been measured.[3] The inverse process, the excitation of a plasmon by a photon, is known as optical plasma-resonance absorption.[4] It has been established experimentally as a dip at the plasma frequency in the transmittance curve of thin Al foils.[5] This minimum occurs only for the p component (E vector parallel to the plane of incidence) at non-normal incidence, while the s component shows no structure at the plasma frequency.

The dip in the spectral transmittance of the p component is partially due to the fact that a plasmon which has been excited by a photon does not necessarily decay into a photon again, but may alternatively be damped by electronic damping.[2] This can be accomplished either by disorganization of the collective motion, leading to an increase in the temperature of the electron gas and subsequently of the lattice, or by an interband transition of one electron. The latter process has been predicted theoretically[6] for plasmons with small wave vector. In this case, if the plasmon energy is greater than the work function, the excited electron may leave the metal. Thus, the decay of a plasmon may give rise to photoemission, which should result in a peak at the plasma frequency in the spectral photoelectric yield. As in the case of the optical plasma resonance, this peak should only appear if the sample is irradiated by p-polarized light at non-normal incidence.

An experimental test of this hypothesis requires a polarized continuum light source in the far ultraviolet. For Al, the peak is expected at 835 Å.[3] In this spectral range, the synchrotron radiation is the most effective light source with the above-mentioned features. In the experiment reported here, the synchrotron radiation of the 6-BeV electron synchrotron at Hamburg (DESY) was used. A normal-incidence monochromator[7] provided monochromatic light from the visible region down to about 400 Å. An Al film about 250 Å thick was evaporated onto a glass slide of 0.2-mm thickness and the slide was mounted as the photocathode of a Bendix Model 306 photomultiplier. The multiplier was then positioned behind the exit slit of the monochromator. The multiplier could be tilted with respect to the optical axis and could be turned so that the plane of in-