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MAGNETIC-DIPOLE CONTRIBUTION TO OPTICAL HARMONICS IN SILVER*

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(Received 2 December 1965)

The nonlinear interaction of light with matter via the Lorentz force has been foreseen for some time,[1-7] but until now has not been demonstrated experimentally. Analysis shows that a second-harmonic polarization proportional to $\vec{E}\times\partial\vec{H}/\partial t$ is produced when light traverses matter. This polarization is longitudinal and will be observable only in experiments involving a discontinuous medium, e.g., in harmonics generated on reflection. Recently Jha[5,7] has shown that an electric quadrupole interaction of the form $\vec{E}\vec{\nabla}\cdot\vec{E}$, such as that observed in calcite,[8] must also be present in nonlinear reflection from a metal. Harmonic light generated by a laser beam reflected from a silver mirror should be the combined effect of both interactions. In this Letter we report their experimental separation, and thus isolation and detection of second-harmonic light originating in a magnetic-dipole term of the form $\vec{E}\times\partial\vec{H}/\partial t$ associated with the Lorentz force. Our results suggest that the conduction-electron plasma in silver is the principal source of the observed second-harmonic light.

We compare our experimental results with the analysis by Jha[7] based on a self-consistent solution of Maxwell's equations for the electromagnetic fields and the classical Boltzmann equation for the distribution function of the conduction electrons in a metal. The nonlinear polarization is found to have the form $\alpha(\vec{E}\times\partial\vec{H}/\partial t)+\beta\vec{E}\vec{\nabla}\cdot\vec{E}$. Let light be reflected from a plane boundary, $x\geqslant 0$, with angle of incidence θ. Let x-y be the plane of incidence and Θ be the angle of $\vec{E}$ relative to the plane of incidence. Since the $\vec{E}\times\partial\vec{H}/\partial t$ polarization is longitudinal, the reflected second harmonic due to the Lorentz force will always lie in the plane of incidence regardless of the angle Θ. The nonvanishing terms of $\vec{E}\vec{\nabla}\cdot\vec{E}$ are $E_x\nabla_xE_x$ and $E_y\nabla_xE_x$, producing a second-harmonic polarization in the plane of incidence, and $E_z\nabla_xE_x$, a polarization parallel to the reflecting boundary. If the incident light beam is polarized perpendicular to the plane of incidence, $\Theta=90°$, ∇_xE_x vanishes and no second-harmonic radiation is produced by the quadrupole effect. The only second-harmonic light produced for this polarization of the incident beam is that due to the Lorentz force, and it is polarized in the plane of incidence. If $\Theta=0°$, $\vec{E}\vec{\nabla}\cdot\vec{E}$ contains components only in the plane of incidence and second-harmonic light produced by the electric quadrupole effect will be plane polarized in the plane of incidence. Therefore, the theory predicts that the only second-harmonic light produced will be that due to the Lorentz force when $\Theta=90°$. Furthermore, for $\Theta=90°$ or $\Theta=0°$, the second-harmonic light produced will be plane polarized in the plane of incidence.

When $\Theta=45°$, we use the Cartesian components, G_{12}, G_{22}, and G_{32}, of the second-harmonic vector potential of the reflected light to find the polarization angle Θ' of the reflected beam. The G's, given by Jha's[7] Eqs. (5.18)-(5.20), are functions of the angle of incidence θ, the polarization angle of the incident light Θ, and the ratio ω_p/ω, where ω_p is the plasma frequency of the conduction electrons in the metal and ω is the frequency of the ruby-laser incident light beam. For $\theta=\Theta=45°$ and $\omega_p/\omega=5$, the theoretical polarization of the reflected harmonic beam is given by

$$G_{32}/\sqrt{2}\,G_{22}=0.30\exp(-0.40i), \qquad (1)$$

indicating that G_{32}, the second-harmonic component perpendicular to the plane of incidence, lags the component in the plane, G_{22}, by 23°. Thus the reflected harmonic light exhibits a small ellipticity. The polarization angle of the reflected harmonic beam is given by the modulus of (1) as $\Theta' = 17°$. Consequently the term $E_z \nabla_x E_x$ of the electric quadrupole effect contributes a component of nonlinear polarization parallel to the reflecting boundary. This component is approximately in phase with $\vec{E} \times \partial\vec{H}/\partial t$ and the other components of $\vec{E}\vec{\nabla}\cdot\vec{E}$ lying in the plane of incidence and is of comparable magnitude. Thus with $\Theta = 45°$, theory predicts that the reflected second-harmonic beam should be polarized at an angle $\Theta' = 17°$ and should exhibit a slight ellipticity.

A calculation may also be made of the relative sizes of the $\vec{E}\vec{\nabla}\cdot\vec{E}$ and $\vec{E}\times\partial\vec{H}/\partial t$ effects by means of Jha's theory. Let $M = R_s/R_p$ be the ratio of the relative second-harmonic generation efficiencies for $\Theta = 90°$ and $\Theta = 0°$. Then M is given as the ratio of the coefficients of the $\sin^4\Theta$ and $\cos^4\Theta$ terms in the expression for the total harmonic intensity given by Eq. (17) of Ref. 5,

$$R^{(2)} = \left(\frac{eE_{\text{inc}}}{m\omega_p c}\right)^2 (5.23\cos^4\Theta - 1.12\cos^2\Theta\sin^2\Theta + 0.16\sin^4\Theta). \quad (2)$$

This gives $M = 0.16/5.23 = 0.031$. It is seen that the theory predicts quantitative values for two basically different measurements, one involving the polarization of the reflected second-harmonic light for several angles Θ, and the other giving an intensity ratio. These theoretical values will now be compared with experiment.

In the initial work on silver,[9] we found a Θ dependence of the relative harmonic intensity consistent with $\cos^4\Theta$. Detection efficiency was low and fluctuations made it impossible to rule out a signal at $\Theta = 90°$ or to detect moderate deviations from a strict $\cos^4\Theta$ law. Recently conditions have been improved and we have consistently been able to detect second-harmonic light at $\Theta = 90°$ which satisfies the usual identification criteria and to make polarization measurements on it. Significant modifications of the earlier procedure include weak focusing on a single silver mirror to make use of the higher coefficient of reflection of silver for light polarized perpendicular to the plane of incidence, and greater detection efficiency. In all cases it has been necessary to avoid incident power densities greater than 5 to 10 MW/cm^2 to achieve repeatable signals.

Polarization measurements made with $\Theta = 90°$ and $\Theta = 0°$ indicate that, as expected, the second-harmonic light is plane polarized in the plane of incidence; see Fig. 1(a). It should be remarked that a residual dipole interaction with symmetry $\vec{E}\vec{E}$, due to surface atoms, could not cause the observed Lorentz-force effect. The incident light was strictly plane polarized, and the accuracy of our knowledge of Θ ($\Theta = 90 \pm 1°$) rules out a possible artifact due to a component of $\vec{E}$ in the plane of incidence. The polarization data shown in Fig. 1(a) suggest that the harmonic signal at $\Theta = 90°$ is indeed due to the $\vec{E}\times\partial\vec{H}/\partial t$ interaction.

Polarization measurements at $\Theta = 45°$ [Fig. 1(b)] show that the second-harmonic light is approximately plane polarized at an angle $\Theta' = 16.5 \pm 0.5°$ in agreement with the theory. The theoretical ellipticity is small enough to have escaped detection. Further, on the basis of twenty independent measurements, the ratio $M = R_s/R_p$ of the generation efficiencies at $\Theta = 90°$ and

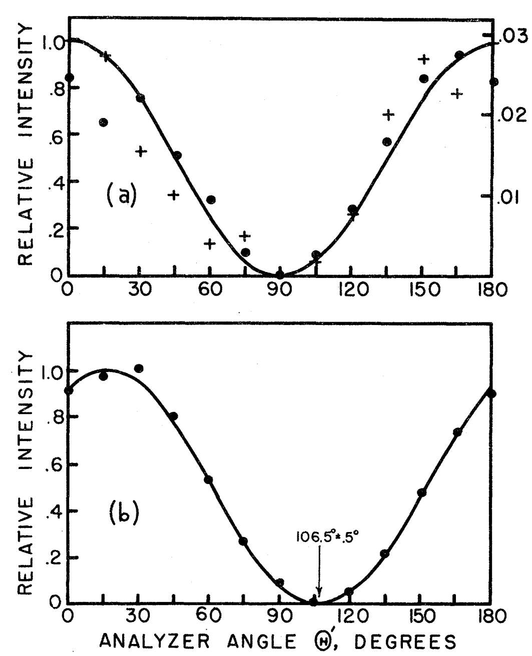

FIG. 1. Polarization of second-harmonic light from silver. Graphs show relative intensity of second-harmonic light from analyzer as a function of analyzer angle Θ' when incident light is polarized as shown. (a) • (left-hand scale): Θ = polarization angle of incident light relative to plane of incidence = 0°. + (right-hand scale): $\Theta = 90°$. (b) $\Theta = 45°$, showing the existence of a harmonic surface current normal to the plane of incidence.

$\Theta = 0°$ was found to be $M = 0.029 \pm 0.007$. Both the polarization and intensity-ratio measurements agree within experimental error with those given in the theory.

However, as emphasized by Jha, the theory contains assumptions which make it only partially valid when ω lies in the visible region. Furthermore, we have assumed $\omega_p/\omega = 5$, which is equivalent to ignoring the effect of interband transitions on the motion of conduction electrons. That this procedure is questionable is shown by the spectral studies of Ehrenreich and Philipp,[10] which show the pronounced effect of the d-band electrons on linear reflectivity. Presumably these bound electrons may contribute through electric quadrupole and magnetic dipole interactions of the same symmetry as those found for the conduction plasma. The apparent plasma resonance, ω_p, in silver for nonlinear interactions would then be a joint response of bound and nearly free electrons. However, it seems quite unlikely from our measurements that a dipole interaction of the form $\vec{E}\vec{E}$ involving surface atoms can make an important contribution. If such a term were dominant, there would be no signal for $\vec{E}$ polarized parallel to the surface, nor would there be a component of harmonic light polarized parallel to the surface for $\Theta = 45°$. In addition, the pronounced surface current demonstrated in Fig. 1(b) proves that the normal component $E_x \nabla_x E_x$ is not the dominant term of $\vec{E}\vec{\nabla}\cdot\vec{E}$. If it were, the reflected harmonic light would always be polarized in the plane of incidence, contrary to observation. Accordingly, Jha's assumption that the nonlinear current normal to the surface can be disregarded is probably correct in the present case. Although it is possible that electric quadrupole or magnetic dipole effects of bound electrons may make a contribution to our observations, the agreement achieved here with a theory based solely on the properties of conduction electrons suggests that the conduction-electron plasma may be the principal source of the second-harmonic signal. Our results, therefore, disagree with the recent interpretation of Bloembergen and Shen,[6] who suggest that the harmonic light from silver is probably due to ion-core electrons at the reflecting boundary. Possibly for germanium and silicon the dipole $\vec{E}\vec{E}$ effect is dominant because of the large nonlinear susceptibility of these crystals. Sooy, Geller, and Bortfield[11] have shown that the effects at semiconductor surfaces under giant-pulse conditions are quite complex.

The authors are indebted to Dr. S. S. Jha for informing them of his latest results and to A. St.Pierre for help in constructing the apparatus. They are also grateful to Professor David Park for many valuable discussions. One of us (F.B.) would like especially to thank the Institute for Solid State Physics at the University of Tokyo for the generous provision of space and time during the preparation of this paper.

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*Work supported by U. S. Army Research Office—Durham, Durham, North Carolina.

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