Giant second harmonic and size effect in ultrasmall metal particles

O. A. Aktsipetrov, I. M. Baranova, S. S. Elovikov, P. V. Elyutin, D. A. Esikov, A. A. Nikulin, and N. N. Fominykh
M. V. Lomonosov State University, Moscow

(Submitted 23 April 1985)
Pis'ma Zh. Eksp. Teor. Fiz. **41**, No. 12, 505–508 (25 June 1985)

An increase by four orders of magnitude has been observed in the gain for the giant second harmonic for metal particles with a radius on the order of 10 Å. The increase results from the influence of size effects on the nonlinear susceptibility and the local-field factor.

The intensification of nonlinear-optics processes at rough metal surfaces, which was first observed for surface-enhanced (or "giant") Raman scattering,[1] results from an increase in the local field due to the excitation of localized surface plasmons[2] and a "lightning-rod effect."[3] Island films of silver exhibit, in addition to the surface-en-

 0021-3640/85/120615-05$01.00

hanced Raman scattering, the generation of a giant second harmonic: The intensity ($I_{2\omega}$) of the second harmonic reflected from a system of small metal particles is several orders of magnitude greater than $I_{2\omega}$ at a smooth silver surface. For island films we have

$$I_{2\omega} \sim (d_m \chi_2 L(2\omega) L^2(\omega) I_\omega)^2,$$

where $d_m = nv$ is the mass thickness, v is the volume of the island, n is the surface density of particles, χ_2 is the quadratic susceptibility, L is the local-field factor, and I_ω is the pump intensity. In the electrostatic approximation, in which the radius of a spherical island satisfies $R \ll \lambda$ (the pump wavelength), we have $L(\omega) = 3/(\epsilon(\omega) + 2)$, and this factor is independent of the radius R [$\epsilon(\omega)$ is the dielectric constant of the metal]. This expression for L holds for an isolated sphere. When collective effects are taken into account, we find a shift of the resonant frequency, at which the condition $\mathrm{Re}[\epsilon(\omega) + 2] = 0$ holds. Accordingly, in the more general case we would have[5] $L = L(\omega, q)$, where q is a filling factor (the fraction of the metal which is in the interior of the film). In the electrostatic approximation, $I_{2\omega}$ is also independent of R; this independence is also observed for island films with $R \gtrsim 100$ Å. At $R < 100$ Å, however, the linear and nonlinear optical properties of the small particles may be changed substantially by size effects, so that there should be changes in the gain for the giant second harmonic.

In this letter we report a study of the influence of size effects on the generation of the giant second harmonic by ultrasmall metal particles with $R \sim 10$–100 Å. For pumping we use the beam from a pulsed Nd:YAG laser with $\lambda = 1064$ nm and $I_\omega \sim 0.5$ MW/cm^2. The second harmonic, at $\lambda = 532$ nm, is detected by the measurement apparatus described in Ref. 3.

The silver island films are deposited in ultrahigh vacuum ($\lesssim 10^{-9}$ torr) on substrates of sodium chloride single crystals on which a film of silicon monoxide ~ 500 Å thick has been deposited. The silver samples are also covered with a protective film of SiO_x, ~ 500 Å thick, after deposition to stabilize the properties of the films. The structural characteristics of the films are studied in a transmission electron microscope. Figure 1 shows a typical micrograph of one of these films, recorded at a magni-

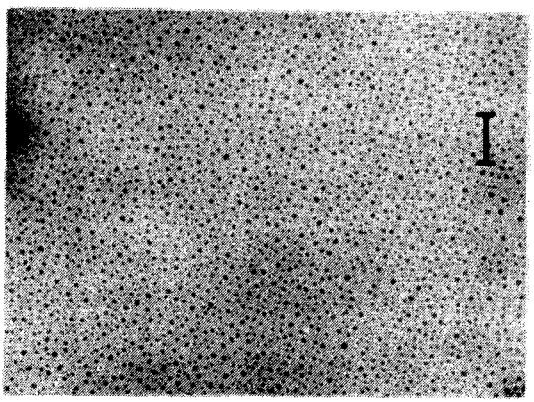

FIG. 1. Structure of a silver island film as observed in a scanning electron microscope. The bar is 200 Å long.

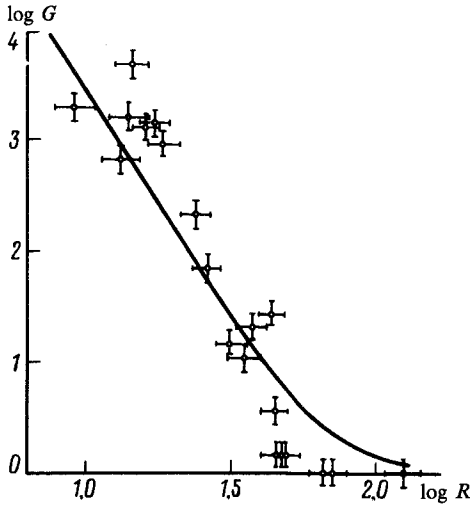

FIG. 2. Points—Experimental values of the logarithm (G) of the normalized intensity of the giant second harmonic as a function of the logarithm of the average island radius (in angstroms); solid curve—the corresponding functional dependence calculated from Eq. (1) with a least-squares fit of the parameter R_a.

fication $\sim 10^6$. The characteristic particle radius R is found by taking an average over several hundred islands.

Figure 2 shows the experimental results on the intensity of the giant second harmonic versus R. The samples differ not only in the average radius R but also in their mass thickness d_m and their filling factor q. Accordingly, the intensity of the second harmonic is normalized by dividing by the quantity $d_m^2 L^2(2\omega,q) L^4(\omega,q)$ to bring out the size effects.

The intensity $I_{2\omega}$ calculated in this manner is divided by the intensity ($I_{2\omega}^0$) of the second harmonic reflected from a smooth surface of monolithic silver [d_m^0 is a length on the order of the skin thickness $\delta \sim 300$ Å; $L^0(\omega) = L^0(2\omega) = 1$]. We see from this figure that at $R \gtrsim 50$ Å the size-effect gain, $G = (I_{2\omega}/d_m^2 L^2(2\omega,q)) L^4(\omega,q))/(I_{2\omega}^0/\delta^2)$, does not depend on the radius of the particles and is not significantly different from unity. This result confirms the normalization method selected. With decreasing particle radius, we observe a substantial increase in the intensity, which reaches four orders of magnitude at $R \sim 10$ Å.

Over the entire region of parameter values in these experiments, the particles satisfy the "metallic condition"[6] $e\mathscr{E}R \gg \Delta_F$, where e is the electron charge, $\Delta_F = E_F/N$ is the average distance between the energy levels near the Fermi surface, E_F is the Fermi energy, and N is the number of conduction electrons. We can therefore ignore changes in the dielectric constant of the metal due to the bounded dimensions of the particle, and we may assume that the local-field factors do not depend on R.

To explain this effect, we should consider a mechanism which increases the quadratic susceptibility of small metal particles beyond that (χ_2^0) of the same volume in bulk metal. In metals with a centrally symmetric lattice, this quadratic susceptibility is zero in the dipole approximation because of parity selection rules. The value of χ_2^0 is determined by the next order of the multipole expansion, quadrupole and magnetic

dipole terms,[7] and is therefore extremely small. In the free-electron model we have $\chi_2^0 = \chi_1/\mathscr{E}_{NL}$, where χ_1 is the linear susceptibility, and $\mathscr{E}_{NL} = 4mc\omega/e$, is the characteristic non-linearity field; here m is the mass of the electron, c is the velocity of light, and ω is the frequency of the external field. At the frequency of a neodymium laser we would have $\mathscr{E}_{NL} = 4\times 10^8$ G.

The increase in χ_2 in small particles may stem from a partial lifting of the parity restriction, with the result that the dipole contribution is no longer zero. A lifting of this sort may be caused by a deviation of the particles from a centrally symmetric shape. Treating the electron as a free particle in a volume bounded by an impenetrable surface—a sphere of radius R—and modulated by a random function with a characteristic amplitude h and a correlation length l ($h,l \ll R$), and using the Migdal method[8] to allow for perturbed boundary conditions, we find the following estimate of the contribution to the dipole quadratic susceptibility caused by an asymmetry, χ_2^a:

$$\chi_2^a \simeq \left(\frac{hl}{Rr_s}\right)^2 \chi_1 \frac{1}{\mathscr{E}_0},$$

where r_s is the radius of the spherical volume per electron, and $\mathscr{E}_0 = m^2e^5\hbar^{-4}$ is the atomic scale of the field.

There is no interference between the dipole and magnetic dipole contributions to the intensity at the frequency of the second harmonic because of the 90° phase shift between the vectors of the corresponding nonlinear polarizations. We can therefore describe the size-effect factor G by

$$G = 1 + \left(\frac{R_a}{R}\right)^4, \tag{1}$$

where

$$R_a^2 \simeq \left(\frac{hl}{r_s}\right)^2 \frac{\mathscr{E}_{NL}}{\mathscr{E}_0}.$$

A least-squares fit of the parameter R_a to the experimental data yields $R_a = 72.4$ Å (Fig. 2). Under the assumption that the expression for G does not contain any numerical constants significantly different from unity, we find the estimate $hl \simeq 25$ Å^2. This estimate is consistent with the assumptions used in the derivation. The general agreement between theory and experiment at $R \lesssim 50$ Å suggests that the mechanism described here is responsible for much of the size-effect increase in the intensity of the second harmonic.

There is another mechanism for a lifting of the parity restriction near the boundary of the metal,[9] involving a deviation from symmetry caused by the self-consistent field that acts on an electron in a layer with a thickness on the order of the Thomas-Fermi screening radius r_{TF}. That mechanism is not manifested under our experimental conditions. An estimate of this "surface" contribution to the quadratic polarizability yields

$$\chi_2^s \simeq \left(\frac{kr_{TF}}{R}\right)\chi_1 \frac{1}{\varepsilon_0} ,$$

where k is a constant on the order of a few units. Setting $k = 3$, we find that χ_2^s outweighs χ_2^a only at $R \gtrsim 100$ Å, where the size-effect intensification is not observed.

We wish to thank L. V. Keldysh, E. M. Dubinin, and D. N. Klyshko for organizing this study and for comments offered in a discussion of the results.

[1]Surface-Enhanced Raman Scattering (Russ. transl. ed. V. M. Agranovich, Mir, Moscow, 1984).
[2]N. Moskovits, J. Chem. Phys. **68**, 4159 (1978).
[3]O. A. Aktsipetrov, I. M. Baranova, E. D. Mishina, and A. V. Petukhov, Pis'ma Zh. Eksp. Teor. Fiz. **40**, 240 (1984) [JETP Lett. **40**, 1012 (1984)].
[4]C. K. Chen, A. R. B. de Castro, and Y. R. Shen, Phys. Rev. **46**, 145 (1981).
[5]V. I. Emel'yanov and N. I. Koroteev, Usp. Fiz. Nauk **135**, 345 (1981) [Sov. Phys. Usp. **24**, 864 (1981)].
[6]L. P. Gor'kov and G. M. Éliashberg, Zh. Eksp. Teor. Fiz. **48**, 1407 (1965) [Sov. Phys. JETP **21**, 940 (1965)].
[7]N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, Phys. Rev. **174**, 813 (1968).
[8]A. V. Migdal, Kachestvennye metody v kvantovoĭ teorii (Qualitative Methods in Quantum Theory), Nauka, Moscow, 1975.
[9]H. W. K. Tom, T. R. Heinz, and Y. R. Shen, Phys. Rev. Lett. **51**, 21, 1983 (1985).

Translated by Dave Parsons