Experimental study of surface-enhanced second-harmonic generation on silver gratings

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We performed an experiment of surface-enhanced second-harmonic generation on silver gratings of various groove depths. Using gratings with constant periodicity (1800 grooves/mm), we measured the intensity of the diffracted orders 0 and -1 at the second-harmonic frequency. This was done by varying the angle of incidence of the pump beam and also testing several different groove depths. We get an enhancement of the second-harmonic intensity by a factor of about 36 as compared to the flat silver case. Our data show that this enhancement, which arises from the surface-plasmon resonance at the pump frequency, depends strongly on the groove depth. In addition, we demonstrate an important and new result: There exists an optimum value of the groove depth for which this enhancement is maximum. A good agreement is found between our measurements and results predicted by the theory of diffraction in nonlinear optics [R. Reinisch and M. Neviere, Phys. Rev. B **28**, 1870 (1983)].

I. INTRODUCTION

Enhancement of the efficiency of nonlinear (NL) optical processes by rough surfaces has been known for a long time.[1] This effect appears in many experiments, such as Raman excitation of surface polaritons,[2] surface-enhanced Raman scattering (SERS) by adsorbed molecules,[3] and surface-enhanced second harmonic generation (SESHG).[4] This enhancement is related to the existence of two mechanisms: chemical interactions between metal and molecules, which occur especially in SERS[3,5] and electromagnetic resonances on rough surfaces.[6]

Only the second mechanism is involved in SESHG on metallic gratings and randomly rough surfaces. Among all the theories[7] dealing with SESHG, the only one which treats the groove depth rigorously is that of Ref. 8. The surprising result predicted by this theory[8] is the existence of an optimum groove depth δ_{opt} for which the enhancement of the efficiency of second harmonic generation (SHG) is maximum. This enhancement arises from the resonant excitation of *nonlocalized* surface plasmons (SP).

Early experimental results have already been published[9] concerning SESHG on a silver grating. In Ref. 9, the emphasis was on the -1 diffracted order at the SH frequency. But any comparison with the corresponding experimental results was impossible since at the time the experiment was performed the computations concerning the theory of Ref. 8 were still in progress.

Now, the computations have been completed. Thus we are in a position to compare the numerical results predicted by the theory of diffraction in nonlinear optics with corresponding experimental measurements. As will be seen in this paper, there is a discrepancy between the measurements reported in Ref. 9 and the theory of diffraction in NL optics.

This prompted us to perform another experiment of SESHG on silver gratings of various groove depths taking into account the results of our recent computations. In this new experiment, we studied not only the -1 diffracted order at the SH frequency (as was the case in Ref. 9), but also the zero one.

The purpose of this paper is to present our data and to compare it with the results predicted by the theory of diffraction in NL optics.[8] It is worth noting that such an experiment in which nonlocalized surface plasmons are involved is different from that performed by Wokaun *et al.*[10]

Indeed, these authors measured the intensity of the second harmonic light generated by metallic island films evaporated on sapphire, as a function of the mass thickness of these islands. They observed a maximum of this intensity for an optimum mass thickness, and they ascribed this effect to the excitation of *localized* surface plasmons. In this kind of experiment, nonlocalized surface plasmons cannot be excited as long as the metal islands do not coalesce. In Ref. 10, SHG by nonlocalized surface plasmons is only briefly considered.

This paper is organized as follows: In Secs. II A and

II B, we describe the experimental apparatus and the method used to detect the SH signal. The measurements performed with the silver gratings are presented in Sec. II C. The end of the paper (Sec. III) is devoted to the comparison between theoretical and experimental results. We also discuss the results published in Ref. 9.

II. EXPERIMENT

A. Experimental setup

The experimental setup is depicted in Fig. 1. We use a Q-switched Nd^{3+}-YAG laser: its wavelength is 1.064 μm, the pulse energy is 100 mJ, the pulse duration is 20 ns, with a repetition frequency of one hertz. The TM polarization (**H** parallel to the grooves of the grating) is achieved with a Glan-Taylor prism. The laser beam is directed onto a silver grating placed on a rotating mount. The outside medium is air. The detector and the associated infrared light filters rotate around the same axis as the grating; the accuracy of the angle measurement is better than 5 min.

As explained in Ref. 8, the infrared incident light is diffracted linearly by the grating. By nonlinear interactions in silver, the second harmonic light is generated and is also diffracted by the grating. In this experiment, we look at the 0 and -1 diffracted orders at the second harmonic frequency. When the external medium is nondispersive (which is the case of air), the pth diffracted order at the pump frequency and the $2p$th diffracted order at second harmonic frequency are diffracted in the same direction.[8] Thus, we must filter the zero order of infrared light to detect the zero-order second harmonic signal. The pump light at 1.064 μm is suppressed using a dichroic mirror M_1 which reflects 99.5% of the infrared light, but which is transparent at $\lambda/2=0.532$ μm, a 1-cm-thick $CuSO_4$ solution cell, and a monochromator.

The filtered light is detected by a photomultiplier (Hamamatsu R-212). To test this part of the experimental setup, we let the laser beam impinge directly on the detection apparatus, without reflection on the grating: no significant signal at $\lambda=1.064$ μm is detected.

The second harmonic signal from the photomultiplier is observed with a 100-MHz storage scope triggered by a 0.5-ns rise time PIN photodiode which detects a small part of the incident laser beam reflected by the dichroïc mirror M_2. In addition, this mirror M_2 is used to eliminate the visible light radiated by the laser-pump flashes. The second harmonic signal from the photomultiplier passes the usual tests:[11] exact SH wavelength, monochromaticity, time correlation with the monitor signal from the PIN photodiode, and collimation along the calculated directions of diffraction.[8]

The peak power delivered by the Nd^{3+}-YAG laser varies from pulse to pulse. About 40 laser shots are needed to obtain a typically adequate standard deviation of 5%. In all the measurements, the SH intensity of the 0 and -1 diffracted order is high enough to be detected without any photon-counting techniques (minimum of 200 reflected photons at $\lambda/2=0.532$ μm which correspond to 10 photoelectrons at the photomultiplier cathode).

B. Sample preparation

The gratings are made by holographic techniques in order to obtain a periodicity of 1800 grooves/mm. We use glass slides coated with low-reflection chrome film and with 0.5 μm of Shipley AZ-1350 photoresist. They are then exposed to an expanded Ar^+ laser beam ($\lambda_{Ar}=4579$ Å) in a Lloyd's mirror interferometric mount. The slides are developed and coated by evaporation at low pressure (10^{-5} Torr), with more than 0.4 μm Ag film. The evaporated silver is of high purity (99.99%) and the film thickness is controlled by a quartz-crystal thickness monitor. After evaporation, the gratings are preserved in a low-pressure air dessication box.

The groove depth is determined optically by using Heitmann's method[12] with a TE polarized He-Ne laser beam. For groove depths less than 600 Å, the accuracy is within 10%. For large groove depth measurements (> 600 Å), we use a scanning electron microscopy (SEM) method,[13] which in addition allows us to observe the groove profiles (Fig. 2).

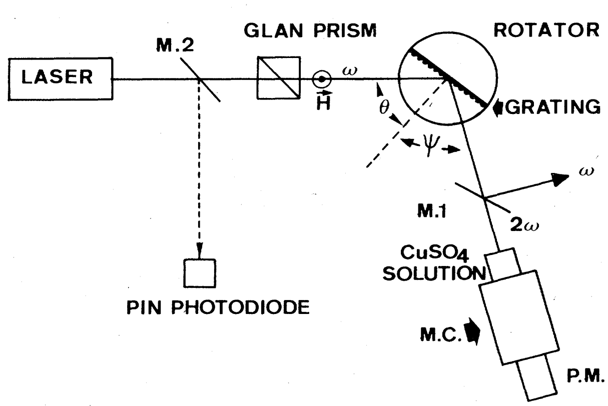

FIG. 1. Schematic of the experimental setup.

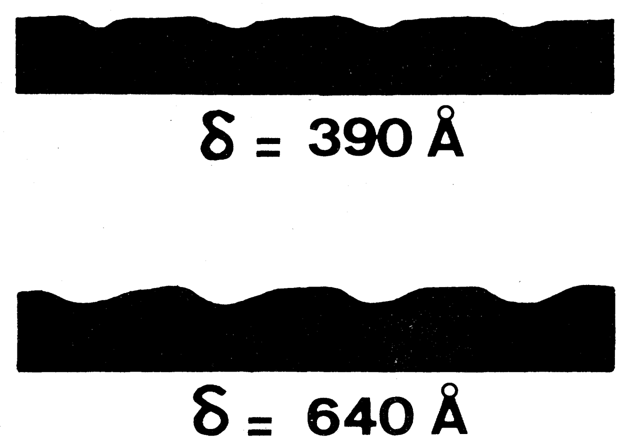

FIG. 2. Electron micrographs showing the groove profiles.

C. Experimental results

We used the following experimental parameters: pump-beam wavelength, $\lambda=1.064\ \mu m$; groove periodicity, $d=0.556\ \mu m$; and angle of incidence of the pump beam close to the angle of SP resonant excitation at the pump frequency. Thus, there is only one propagating diffracted order (the 0 one) at the pump frequency and two diffracted orders (0 and -1) at the SH frequency.

We measured the power densities $P_{-1}(2\omega)$ and $P_0(2\omega)$ of the diffracted orders -1 and 0. These densities are normalized by the square of the power density $P(\omega)$ of the incident pump beam. We define

$$R_{-1}(2\omega)=P_{-1}(2\omega)/P^2(\omega)$$

and

$$R_0(2\omega)=P_0(2\omega)/P^2(\omega)\ .$$

The values of R_{-1} and R_0 are independent of the cross section and of the power of the incident pump beam.

We performed the following measurements:

(i) For a given groove depth δ and for a given angle of incidence θ corresponding to detectable values of R_{-1}, we measured the angular distribution of R_{-1}. These measurements were repeated for other θ's (Fig. 3).

(ii) This allowed us to get, for this groove depth, the θ dependence of the R_{-1} peak values. We then obtained the set of curves of Fig. 4 by varying the groove depth δ.

(iii) Next, we considered the peak values R_{-1M} of each curve of Fig. 4: Fig. 5 is the plot of R_{-1M} as a function of δ.

The peak power R_{0M} of the 0 diffracted order as a function of δ is also reported in Fig. 5. The corresponding data have been obtained by the same procedure as that described in steps (i), (ii), and (iii) for the -1 diffracted order.

Step (i) is due to the fact that the incidence angle θ_p for which the SH signal is maximum is not exactly equal to the incidence angle θ_{res} for which the surface plasmon at $\lambda=1.064\ \mu m$ is resonantly excited.[14] Presumably, this angular shift arises from the losses of silver.

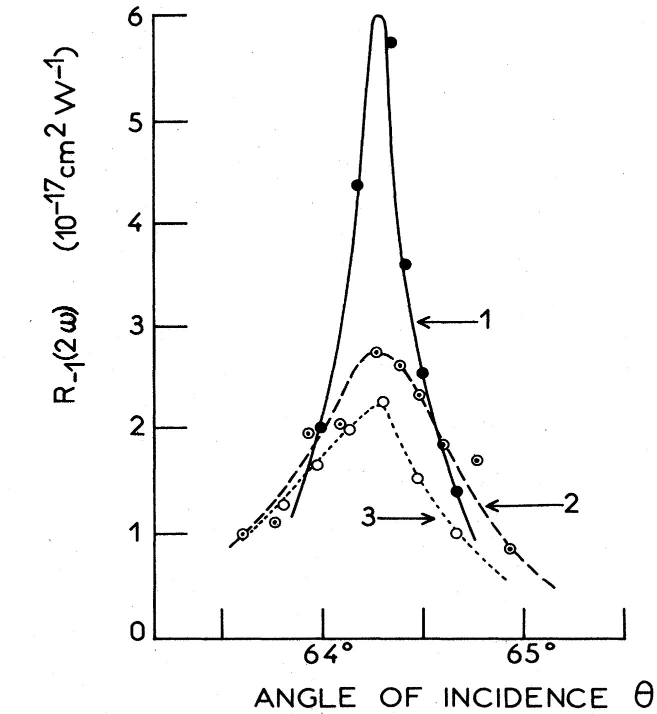

FIG. 4. $R_{-1}(2\omega)$ as a function of θ. Each curve corresponds to a given groove depth: curve 1 corresponds to $\delta=230$ Å; curve 2 to $\delta=350$ Å; curve 3 to $\delta=460$ Å. For each point, the uncertitudes are $\Delta\theta=5'$ and $\Delta R_{-1}=0.6\times10^{-17}\ cm^2\,W^{-1}$.

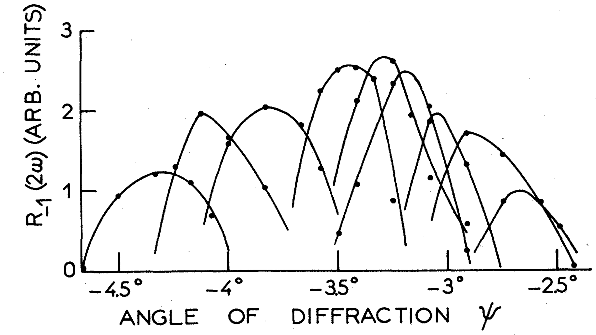

FIG. 3. $R_{-1}(2\omega)$ as a function of the angle of NL diffraction ψ. The points correspond to measured values. For each measurement, the uncertitudes are $\Delta\psi=3'$ and $\Delta R_{-1}(2\omega)=0.6\times10^{17}\ cm^2\,W^{-1}$. $d=5556$ Å and $\delta=350$ Å. Each curve is obtained by keeping constant the angle of incidence and varying the angle ψ. The angle ψ is the angle between the grating normal and the detector. The set of curves is obtained by varying the angle θ. The curve for which the SH signal is maximum corresponds to $\theta=64.5°$.

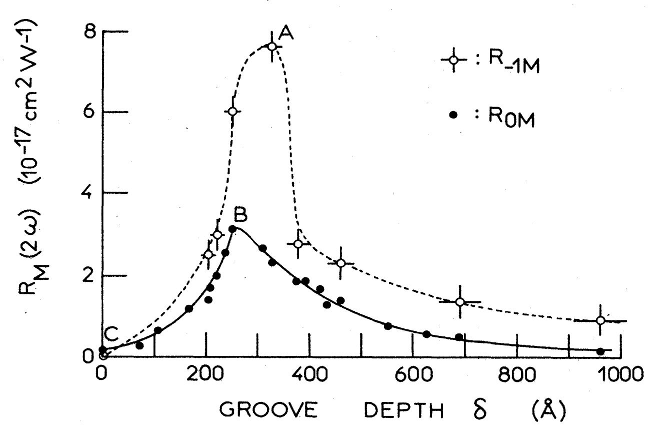

FIG. 5. $R_{-1M}(2\omega)$ and $R_{0M}(2\omega)$ for several values of δ. For the sake of clarity, dotted and continuous lines join the experimental points. These lines do not correspond to computed curves.

III. DISCUSSION

A. Main results of the theory of Ref. 8

In Ref. 8, the authors developed an electromagnetic theory of diffraction in NL optics, studying NL interactions of the kind $\omega_3=\omega_1+\omega_2$ on a grating ruled on a NL material. Maxwell equations are solved everywhere in space taking into account fully the diffraction of the pump beams. In each homogeneous region (above and below the grating), the fields at the pump frequencies ω_1 and ω_2 are described by a superposition of plane waves. In the modulated region (the grating of depth δ), the fields at frequency ω_1 and ω_2 are Fourier expanded. Solving for the boundary conditions allows us to compute the fields at frequency ω_1 and ω_2 everywhere, leading thus to the NL polarization at frequency ω_3. This allows us to obtain the expression of the electromagnetic field at the signal frequency ω_3 (here second harmonic frequency).

This theory is rigorous in the sense that the groove depth of the grating is not considered as a perturbative parameter. The calculation has a wide range of applications. Indeed, it is valid for bare and coated gratings and also for TE and TM polarization of the pump beams and of the signal.

The main results predicted by this theory are as follows: (1) Derivation of the NL grating formula which allows the determination of the directions of propagation of the diffracted orders at the signal frequency. (2) Existence of electromagnetic resonances, not only at the pump frequencies, but also at the signal frequency. Depending on the nature of the gratings (bare or coated), these resonances can be of the surface-polariton type or of the guided-wave type. (3) Enhancement of the efficiency of the NL process (here SHG) through these resonances. (4) Existence of an optimum value of the groove depth for which this enhancement is the strongest. This last result is a direct consequence of the fact that the groove depth is rigorously taken into account.

B. Comparison of the theory with the experiment

Figures 4 and 5 exhibit some important results. Figure 4 shows the strong θ dependence of R_{-1} and the existence of a value θ_p of θ for which R_{-1} is maximum. Note that the width at half-maximum height of the curves is very small (of the order of 0.5°). Thus, the angular dependence of SHG exhibits a very sharp resonance. Our main result corresponds to Fig. 5. It clearly exhibits the existence of two optimum values $\delta_{opt,0}$ and $\delta_{opt,-1}$ of the groove depth for which the power of the 0 and -1 diffracted orders at SH frequency is maximum. We get slightly different values of δ_{opt}, namely,

$$\delta_{opt,0}=250 \text{ Å and } \delta_{opt,-1}=300 \text{ Å} .$$

Note that the peak value of R_{-1M} is greater than that of R_{0M}. The optimized enhancement of the SH power in the 0 and -1 diffracted orders (points A and B of Fig. 5) is about 15 and 36 as compared to the measured SH power for the flat interface case (point C of Fig. 5).

Let us now consider the corresponding theoretical results (Figs. 6 and 7). The similarity between the curves of Figs. 4 and 5 on the one hand and Figs. 6 and 7 on the other hand is remarkable. We see that the results predicted by the theory of diffraction in NL optics[8] agree well with the experimental measurements: the curves R_{-1} as a function of θ (Fig. 6) show nearly the same shape as the corresponding experimental one; there exists a value $\delta_{opt,0}$ and $\delta_{opt,-1}$ of δ for which R_{0M} and R_{-1M}, respectively, are maximum (Fig. 7); and the enhancement at the SH frequency is of the order of 5 for the 0 diffracted order and of the order of 11.5 for the -1 diffracted order (Fig. 7). In addition, the curves (Fig. 7) exhibit the same shape, especially the asymmetrical feature, as the experimental results of Fig. 5 do.

However, there are some differences between the theory and the experiment: (a) a shift between the theoretical

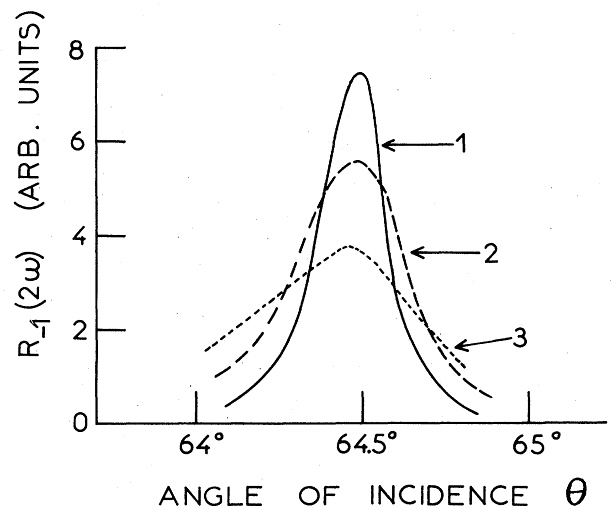

FIG. 6. Computed values of $R_{-1}(2\omega)$ versus the angle of incidence θ. Each curve corresponds to a given groove depth: curve 1 corresponds to $\delta=230$ Å; curve 2 to $\delta=350$ Å; curve 3 to $\delta=460$ Å.

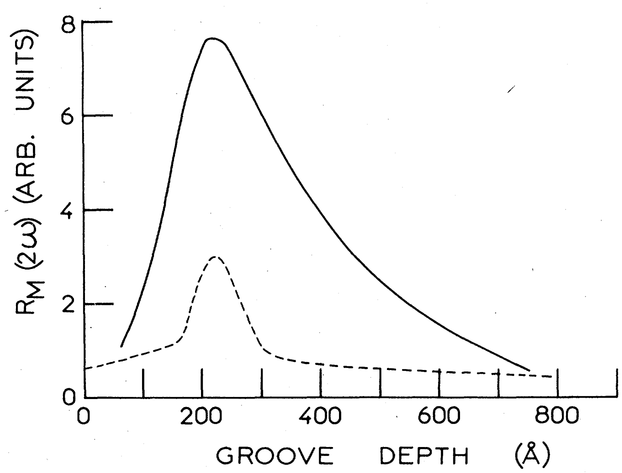

FIG. 7. Computed values of $R_{-1M}(2\omega)$ and $R_{0M}(2\omega)$ as a function of the groove depth δ. The dotted curve corresponds to the 0 diffracted order, the continuous curve to the -1 diffracted order.

and the experimental δ dependence of R_{-1M} and R_{0M} and (b) the measured value of the enhancement is greater than the computed value. This also explains the differences between the R_{-1} peak value of Fig. 6 and the corresponding data of Fig. 4.

Two reasons may explain these differences: (1) the difficulties concerning the nonlinear optical response of metal surfaces[15] and (2) the fact that the grating profiles are not exactly sinusoidal (Fig. 2).

C. Comparison with the results of Ref. 9

Let us consider Fig. 5 of Ref. 9 which, for sake of convenience, has been reproduced in this paper (Fig. 8). We see that the curve of Fig. 8 exhibits two bumps which appear neither in Fig. 7 nor in Fig. 5. This discrepancy may be explained as follows: In the experiment reported in Ref. 9, the value θ_{res} of θ (i.e., the value of θ for which SP resonance occurs at the pump frequency) has been determined with a low accuracy ($\pm 15'$), R_{-1} being measured for the corresponding value of θ. This lack of accuracy in the determination of θ_{res} comes from the fact that at the time the experiment of Ref. 9 was performed, the computer calculations were still in progress, and the authors were not aware of the very small linewidth of the R_{-1} curves.

To check this explanation (i.e., the importance of an accurate determination of θ_{res}), we have computed the values of R_{-1} for the angles $\theta_{res-15'}$ and $\theta_{res}+15'$ as a function of δ: we get curves *D* and *E* of Fig. 9. Also reported in Fig. 9 is the R_{-1M} (curve *F*).

We see that curves *E* and *F* (and *D* and *F*) separate as δ approaches δ_{opt}. This is due to the fact that the linewidth of the curves $R_{-1}(\theta)$ decreases when δ tends toward δ_{opt}. Curve *D* [i.e., $R_{-1}(\theta_{res}-15')$] lies within curves *E* and *F*, i.e., does not lead to the lowest value of R_{-1}, because the curves $R_{-1}(\theta)$ (Fig. 4) exhibit a slight asymmetry: the decrease of R_{-1} as a function of θ is slower for $\theta<\theta_{res}$ than for $\theta>\theta_{res}$.

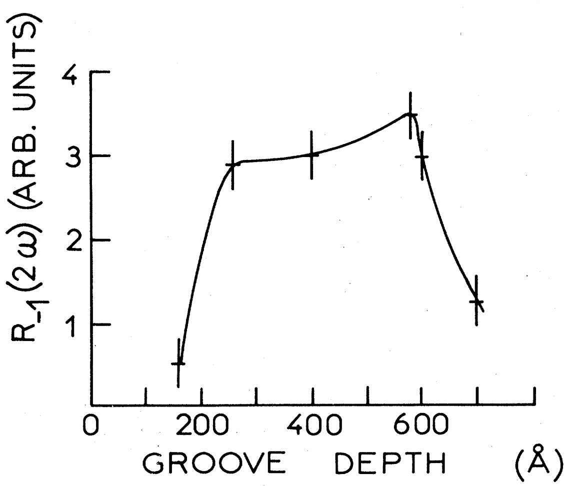

FIG. 8. Measured SH signal versus the groove depth of the grating in the -1 diffracted order: data reprinted from Ref. 9.

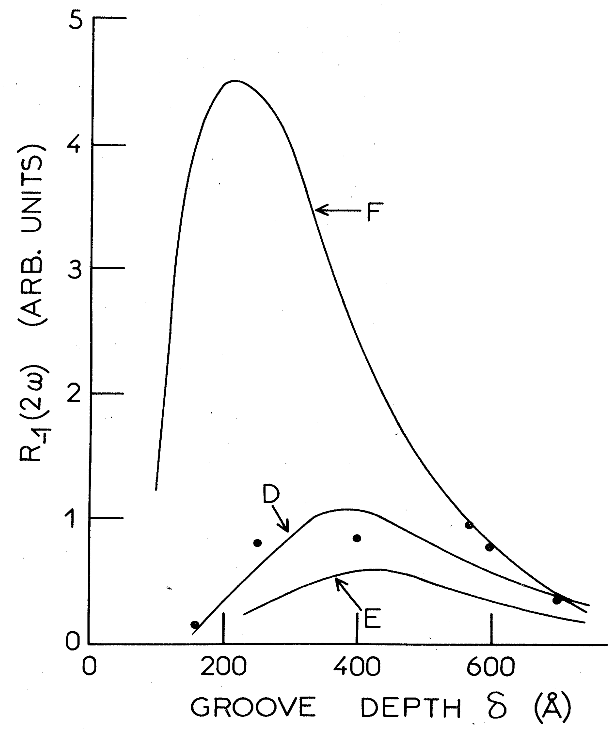

FIG. 9. $R_{-1}(2)$ versus the groove depth δ. Curve *F* has been computed for the optimum angle of incidence θ_p. Curve *D* has been computed for an angle of incidence $\theta=\theta_p-15'$ and curve *E* for $\theta=\theta_p+15'$. The points correspond to the experimental data of Ref. 9. Notice that all these points (measured with an uncertitude $\Delta\theta=\pm 15'$) lie between curves *E* and *F*. The latter corresponds to the maximum theoretical SH signal.

Figure 9 has the following meaning: determining θ_{res} within an accuracy of $\pm 15'$ and measuring R_{-1} for the corresponding value of θ, leads to values of R_{-1} which have to lie between curves *F* and *E*. This is indeed the case when the experimental values of Fig. 8 are reported in Fig. 9.

IV. CONCLUSION

We have performed an experiment of diffraction in NL optics, namely, SHG at silver gratings. The measurements were done on the two propagating diffracted orders (0 and -1) at the SH frequency. Special care has been devoted to the θ dependence of R_0 and of R_{-1}. In our opinion, the most important experimental result is the demonstration of optimum values of the groove depth for which we get the highest values of R_0 and R_{-1}. It is worth noting that these peak values correspond to enhanced SHG as compared to the flat-surface case.

Thus, we see that the phenomenon of SESHG appears as a special case of diffraction in NL optics, namely when electromagnetic resonance occurs: we have considered the case where there is a nonlocalized SP resonance at the pump frequency.

We have shown that the results predicted by the theory of Ref. 8, especially the existence of δ_{opt}, agree well with the data reported in this paper. In addition, we could explain the special shape of the curve of Fig. 8. Thus our experimental results can be considered as a check of the validity of the theory of diffraction in NL optics.[8]

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[1]M. Fleischmann, P. J. Hendra, and A. J. McQuillan, Chem. Phys. Lett. **26**, 163 (1974).

[2]S. Ushioda, A. Aziza, J. B. Valdez, and G. Mattei, Phys. Rev. B **19**, 4012 (1979).

[3]*Surface Enhanced Raman Scattering,* edited by R. K. Chang and T. E. Furtak (Plenum, New York, 1982).

[4]C. K. Chen, A. R. B. de Castro, and Y. R. Shen, Phys. Rev. Lett. **46**, 145 (1981).

[5]F. W. King, R. P. Van Duyne, and G. C. Schatz, J. Chem. Phys. **69**, 4472 (1978).

[6]R. Gerstern and A. Nitzan, J. Chem. Phys. **73**, 3023 (1980); S. S. Jha, J. R. Kirtley, and J. C. Tsang, Phys. Rev. B **22**, 3973 (1980).

[7]G. S. Agarwal and S. S. Jha, Phys. Rev. B **26**, 4013 (1982); K. Arya, *ibid.* **29**, 4451 (1984); G. A. Farias and A. A. Maradudin, *ibid.* **30**, 3002 (1984).

[8]R. Reinisch and M. Neviere, Phys. Rev. B **28**, 1870 (1983).

[9]R. Reinisch, G. Chartier, M. Neviere, M. C. Hutley, G. Clauss, J. P. Galaup, and J. F. Eloy, J. Phys. (Paris) Lett. **44**, L1007 (1983).

[10]A. Wokaun, J. G. Bergman, J. P. Heritage, A. Glass, P. F. Liao, and D. H. Olson, Phys. Rev. B **24**, 849 (1981).

[11]H. Sonnenberg and J. Heffner, J. Opt. Soc. Am. **58**, 909 (1968); N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, Phys. Rev. **174**, 813 (1968).

[12]D. Heitmann, Optics Commun. **20**, 292 (1977).

[13]J. Moreland, A. Adams, and P. K. Hansma, Optics Commun. **45**, 11 (1983).

[14]M. Neviere and R. Reinisch, Phys. Rev. B **26**, 5403 (1982).

[15]See the second paper of Ref. 11. See also J. Rudnick and E. A. Stern, Phys. Rev. B **4**, 4274 (1971); J. E. Sipe, V. C. Y. So, M. Fukui, and G. I. Stegeman, *ibid.* **21**, 4389 (1980).