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Optical second-harmonic generation with surface plasmons in noncentrosymmetric crystals

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We report an extensive investigation of optical second-harmonic generation (SHG) with the simultaneous excitation of the surface-plasmon (SP) mode at the interface between a metal and a nonlinear piezoelectric crystal. The birefringence of appropriately oriented potassium dihydrogen phosphate (KDP) crystals is utilized to demonstrate both quasi-phase-matched reflected SHG and transmitted SHG with fundamental SP excitation. The effect on the SHG resonances of the softness of the KDP crystal is discussed. Resonant SHG with fundamental SP excitation is observed for Al- and Ag-metal films on variously oriented quartz crystals. The source of the SHG for the *X*-cut orientation is the nonlinear crystal while for the *Z*-cut orientation it is the metal film. This latter result indicates that the recent observations of DeMartini *et al.* [Phys. Rev. B **23**, 3797 (1980)] must be reinterpreted. In all our experiments, even including those in which a crystal with a large nonlinear susceptibility such as $LiIO_3$ is utilized, the predicted SHG resonance due to the nonlinearly excited harmonic SP mode is always masked by the nonresonant SHG contribution from the metal itself.

I. INTRODUCTION

During the past several years there has been continued interest in utilizing nonlinear optical phenomena to study surface electromagnetic waves at the interface between a negative and a positive dielectric medium.[1] A resonance in the reflected second-harmonic generation (SHG) of ruby laser light from a thin-silver-film—air interface due to the excitation of the fundamental surface-plasmon (SP) mode in the Kretschmann configuration was first reported by one of the present authors (H.J.S.).[2] Demartini and Shen predicted and observed[3] the nonlinear generation of an infrared surface-polariton mode in GaP using optical difference frequency mixing followed by up-conversion. The same authors used SHG to generate surface exciton polaritons[4] in ZnO which were detected through surface-roughness scattering. An enhancement of 3 orders of magnitude in the reflected SHG due to the fundamental SP excitation from a thin silver film evaporated on an *X*-cut-quartz crystal was observed by the present authors.[5] Observation of the 5 orders of magnitude smaller SHG resonance due to harmonic SP excitation was masked by SHG from the silver-prism interface for both *p* and *s* polarization. Chen *et al.*[6] have observed SHG mixing due to counterpropagating surface plasmons on a silver film and also nonlinear mixing of four surface-plasmon waves in a coherent anti-Stokes Raman spectroscopy (CARS) experiment.[7] DeMartini *et al.*[8] have reported observing SHG with SP excitation at an aluminum-quartz interface. Recently the present authors have demonstrated the sharply resonant SHG due to the excitation of the long-range surface-plasmon mode on both sides of a thin silver film[9] evaporated on a quartz crystal.

In this paper we present results on a series of SHG experiments with SP excitation at a single interface between a metal film and a nonlinear crystal. The first group of experiments involves surface plasmons generated at the interface between a silver film and the birefringent crystal potassium dihydrogen phosphate (KDP). In one orientation of the KDP crystal quasi phase matching in reflection is observed when the harmonic critical angle matches the angle for fundamental surface-plasmon excitation. In a second orientation the critical angle for the harmonic is less than the angle for the fundamental surface plasmon, and thus transmitted SHG which is driven by an evanescent SP wave may be observed propagating from the side of the crystal.

The second group of experiments involves aluminum films deposited on *X*-cut- and *Z*-cut-quartz crystals. The motivation for these particular experiments was to reproduce the recent results reported by DeMartini[8] on reflected SHG resonances associated with both fundamental and harmonic SP modes. We find that for an appropriately oriented *Z*-cut-quartz crystal the fundamental SP resonance is due only to the surface nonlinearity of the aluminum film, and that for an incident *s*-polarization fundamental wave on the same crystal the harmonic SP resonance is not observed. Both these results are consistent with our theoretical calculations of SHG due to crystal nonlinearities and metal-surface nonlinearities. Finally we report on a series of experiments in which silver and aluminum films were evaporated on a LiIO crystal, the nonlinear susceptibility of which is an order of magnitude greater than that of quartz.[10] No clear evidence of excitation of a harmonic SP mode is observed.

This paper contains four sections. In Sec. II we outline the theory for SHG with SP excitation from noncentrosymmetric crystals. In Sec. III we describe the experiments and discuss the experimental results. Our findings are summarized in Sec. IV.

II. THEORY

The surface-plasmon mode[11] is a transverse-magnetic (TM) electromagnetic wave propagating along the interface between two infinite isotropic media, one with a negative dielectric constant and the other with a positive dielectric constant. The wave vector k_p of the mode parallel to the interface is given by

$$k_p = \frac{\omega}{c} \left[\frac{\epsilon \epsilon'}{\epsilon + \epsilon'} \right]^{1/2} , \tag{1}$$

where ω is the angular frequency and ϵ and ϵ' are the dielectric constants of the two media. The amplitude of the wave is attenuated exponentially in the direction normal to the boundary. SP waves may be directly coupled only with evanescent waves from a high-index prism at the angle of incidence for SP excitation θ_p such that $k_p = (\omega/c)n \sin\theta_p$, where n is the index of refraction of the prism. For a thin metal film on a uniaxial crystal the dispersion relation is more complicated.[12]

A detailed description of SHG in total internal reflection at a single nonlinear interface has been given by one of the authors (H.J.S.).[13] By extending this analysis, the reflected SHG with SP excitation may be easily calculated. Consider an electromagnetic wave, p polarized, incident from a high-index prism, medium 1, through a semiopaque metal film, medium 2, into a nonlinear optical crystal, medium 3, as shown in Fig. 1. The amplitude of the fundamental wave inside the crystal is determined by the appropriate linear Fresnel transmission factor through the metal film. The fundamental field in the nonlinear crystal drives a nonlinear polarization wave which radiates a second-harmonic wave. The ratio of the reflected second-harmonic irradiance to the square of the incident fundamental irradiance in air, $\mathscr{R}$, is given by

$$\mathscr{R} = |F^L|^4 |F_R^{\mathrm{NLP}} F^{\mathrm{NLR}}|^2 T . \tag{2}$$

F^L is the linear transmission factor which describes the relative amplitude of the fundamental laser field inside the nonlinear crystal and is given by

$$F^L = t_{12} t_{23} e^{+ik_{2z}d} / (1 + r_{12} r_{23} e^{+2ik_{2z}d}) . \tag{3}$$

Here r_{12} and r_{23} are the linear Fresnel reflection-amplitude factors[14] for p-polarized light at the prism-metal and metal-crystal interfaces, respectively; t_{12} and t_{23} are the Fresnel transmission-amplitude factors at the same respective boundaries; k_{2z} is the normal component of the fundamental wave vector in the metal film of thickness d. Near the angle for SP excitation given by Eq. (1), the denominator of F^L is a minimum, and for a silver film with incident 1.06-μm radiation the amplitude of the electromagnetic wave in the nonlinear crystal is enhanced by over an order of magnitude. For an s-polarization incident wave Eq. (3) remains formally the same, but of course there is no SP resonance. The next set of parentheses contains the total nonlinear Fresnel factor which is further factored into two components. The first factor F_R^{NLP} describes the reflection of the harmonic SP mode excited in the piezoelectric crystal and is given by

$$F_R^{\mathrm{NLP}} = T_{32} T_{21} e^{+iK_{2z}d} / (1 + R_{21} R_{32} e^{+i2K_{2z}d}) . \tag{4}$$

The capital letters have a similar meaning to the lowercase letters, but are now interpreted at the second-harmonic frequency. The second factor F^{NLR} is very close to the nonlinear reflection factors given by Bloembergen and Pershan.[15] This latter factor describes the enhancement of reflected SHG near the critical angle for total internal reflection. The nonlinear reflection Fresnel factor for the cases of the nonlinear polarization source polarized parallel and perpendicular to the plane of the incidence can be written as

$$F_{\parallel}^{\mathrm{NLR}} = \frac{2\pi(2\omega/c)^2}{K_3 K_{3z}} \frac{K_{3x} \tilde{P}_z^{\mathrm{NLS}} + K_{3z} \tilde{P}_x^{\mathrm{NLS}}}{2k_{3z} + K_{3z}} \tag{5a}$$

and

$$F_{\perp}^{\mathrm{NLR}} = \frac{2\pi(2\omega/c)^2}{K_3 K_{3z}} \left[\frac{K_{3z} - 2k_{3z}}{K_{3z} + K_{2z}} \right] \tilde{P}_y^{\mathrm{NLS}} , \tag{5b}$$

respectively. Here all the wave vectors with subscript 3 are evaluated in the nonlinear crystal, the small letters refer to quantities at the fundamental angular frequency, ω, and the capital letters to harmonic quantities. $\tilde{P}_x^{\mathrm{NLS}}$ and $\tilde{P}_z^{\mathrm{NLS}}$ are the normalized components of the nonlinear polarization source parallel and perpendicular, respectively, to the crystal face in the plane of incidence as shown in Fig. 1, while $\tilde{P}_y^{\mathrm{NLS}}$ is perpendicular to the plane of incidence. Note that x, y, and z do not refer to crystallographic directions in the nonlinear crystal. The common factors of $|F^L|^2 E^2(\omega)$ have been factored from the standard nonlinear polarization source terms to define the normalized quantities given above. The second-order nonlinear polarization tensor element and the fundamental field geometric projection factors are contained in each of these normalized quantities. (Explicit expressions for $\tilde{P}_x^{\mathrm{NLS}}$, $\tilde{P}_y^{\mathrm{NLS}}$, and $\tilde{P}_z^{\mathrm{NLS}}$ will be given in the appropriate experimental sections.) Finally the last factor, T, contains the appropriate transmission factors for the laser radiation entering the prism from air, the harmonic radiation exiting the prism, and the change in beam cross section due to nonlinear reflection. It is understood that all the Fresnel factors appearing in Eqs. (3) and (4) must be written in terms of the appropriate ordinary and extraordinary dielectric functions of the uniaxial crystals.

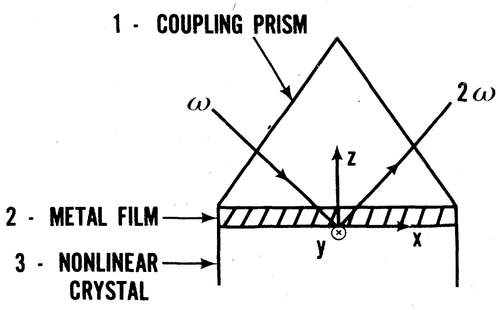

FIG. 1. Kretschmann geometry for SHG from nonlinear crystals with SP excitation.

For the transmission SHG experiment with fundamental SP excitation, the ratio of the transmitted SHG irradiance in air to the square of the fundamental irradiance, $\mathscr{T}$, is given by an expression similar to Eq. (2) with all R

subscripts and superscripts replaced by T. The form of the linear Fresnel factor remains unchanged, but the nonlinear transmission Fresnel factors become

$$F_T^{\mathrm{NLP}}=(1+R_{12}\tilde{R}_{23}e^{+i2K_{2z}d})/(1+R_{21}R_{32}e^{+i2K_{2z}d}) \tag{6}$$

and

$$F_\perp^{\mathrm{NLT}}=\frac{4\pi(2\omega/c)^2\tilde{P}_y^{\mathrm{NLS}}}{K_3^2-(2k_3)^2}\frac{K_{2z}+2k_{3z}}{K_{2z}+K_{3z}}\ , \tag{7}$$

where we have defined

$$\tilde{R}_{23}=\frac{K_{2z}-2k_{3z}}{K_{2z}+2k_{3z}}\ . \tag{8}$$

The transmission factor is modified to account for the transmission of the SHG through the side face of the nonlinear crystal.

There exists a low-level background SHG in these experiments due to that produced by the metal at the prism-metal interface. The interference of this source of SHG with that of the nonlinear crystal is important in several of the experiments, and thus it is necessary to calculate this contribution. A review of SHG from metal surfaces has been given recently by Sipe and Stegeman.[16] Sipe *et al.*[17] have published a theory of SHG due to a free-electron gas which includes hydrodynamic effects and divides the metal into bulk and selvedge regions. Since the linear optical properties of the silver and aluminum films in the 1- and 0.5-μm regions can be described by a free-electron model,[18] we adopt this nonlinear free-electron model as a means of estimating the contribution of the metal-surface SHG sources. The appropriate formulas used in our calculations which are explicitly given in Sec. III of Ref. 17 are too detailed to reproduce here. Our only modifications are to include the entrance and exit prism transmission factor T and to set the Rudnick and Stern[19] phenomenological factors a and b to $+1$ and -1, respectively. A separate experimental determination of the factor a in silver and aluminum films has been performed by the present authors.[20]

Finally we note that in the experiments a thin dielectric liquid layer is included for optically contacting the prism to the evaporated metal film. This additional optical layer was actually included in our theoretical computer code, but for reasonable values of the layer thickness (less than 500 Å), it produced no significant change in any of our theoretical curves where the index of refraction of the nonlinear crystal was less than that of the liquid layer; therefore, we have not included this layer in the formulas presented in this section. For the case where the above inequality is reversed and the effect of the liquid layer becomes significant, the full calculation was used.[21]

III. EXPERIMENTAL RESULTS AND DISCUSSION

The source of the fundamental wave was a mode-locked Nd glass laser which provided a 100-ns pulse train of total energy of 30 mJ with an area of 5 mm^2. The peak power per pulse is estimated to be 100 MW. By passing the radiation through a set of polarizers, either p or s polarization could be selected. A glass beam splitter then directed a fraction of the laser radiation to a fixed-z-axis quartz crystal which provided a monitor level of SHG. The main laser pulse, which was attenuated by factors of up to 2 orders of magnitude, was incident on the prism assembly, which was mounted on a rotating platform that could be continuously adjusted to within 0.05° increments. The specularly reflected SHG, which passed through a $CuSO_4$ cell and a narrow-band interference filter, was detected by an EMI 9635 photomultiplier. The two pulses from the signal and monitor channels were processed in an analog-to-digital converter to directly display a numerical output. Generally 5—10 laser shots were observed for each data point. The specular nature of all harmonic signals was checked by scanning in front of the signal photomultiplier a narrow slit which was offset from the specularly reflected fundamental by an amount calculated using the nonlinear Snell's law.[13] The correct wavelength of the harmonic signal was verified by using interference filters at other wavelengths. An equilateral sapphire coupling prism was used for the reflection KDP experiment, while a right isosceles rutile coupling prism was used for all the other experiments unless specified otherwise. The c axis of the rutile and sapphire prisms were both perpendicular to the plane of incidence in order to ensure that the incident p-polarized radiation propagated as an ordinary wave inside the prism. The metal (99.99% pure) films were evaporated onto the nonlinear crystals at a pressure of 5×10^{-6} Torr and the thickness of the films was measured to within 10% by a Sloan DTM-200 quartz digital thickness monitor. Optical contact between the hypotenuse face of the prism and the metal film was accomplished with a high-index liquid, 1-bromonapthalene. This coupling technique was checked by visually observing the attenuated-total-reflection (ATR) minimum at the SP excitation angle of the He-Ne laser. Observation of the linear ATR on a co-evaporated prism was used to independently check the film thickness. The relevant linear and nonlinear optical constants for all the optical materials used in these experiments are summarized in Table I.

In this investigation of SHG with surface plasmons, we were interested in studying not only the angular dependence but also the quantitative peak response due to the SP resonance. The basic comparison between theory and experiment was made by first performing a Maker experiment,[22] i.e., measuring, in the same apparatus, the SHG in transmission from a wedged, Z-cut-quartz crystal. The theoretical ratio of the transmitted second harmonic power to the square of the fundamental power for such an experiment is well known.[23] We then chose for the standard SHG with SP excitation experiment the one in which a 550-Å-thick silver film is evaporated on an X-cut-quartz crystal. The result for this latter experiment is shown by the solid dots in Fig. 2 where the ordinate is the ratio of harmonic power to the square of the fundamental power on a logarithmic scale and the abscissa is the interior angle of incidence at the base of the coupling rutile prism. We then calculated the ratio of the experimentally observed peak SHG in this SP experiment to the SHG in the Maker experiment. This experimental ratio was compared to the theoretically calculated ratio and found to agree to within a factor of 2. The error is not due to sta-

TABLE I. Optical constants.

	Material	Reference	Wavelength (μm)	Ordinary refractive index	Extraordinary refractive index	Nonlinear susceptibility (10^{12} m/V)
Coupling prisms	Rutile	26	1.06	2.481	2.744	
			0.53	2.673	2.985	
	Sapphire	26	1.06	1.756	1.760	
			0.53	1.771	1.775	
Nonlinear crystals	Quartz	23	1.06	1.534	1.543	$d_{11}=0.40$
			0.53	1.547	1.556	
	KDP	23	1.06	1.494	1.460	$d_{14}=0.47$
			0.53	1.513	1.461	
	Lithium iodate	23	1.06	1.860	1.719	$d_{31}=5.2$
			0.53	1.901	1.750	
					Complex dielectric constants	
Metals	Silver	24	1.06		$-67+2.44i$	
			0.53		$-12+0.33i$	
	Aluminum	26	1.06		$-95+33i$	
			0.53		$-33-+20i$	

tistical fluctuation in the data but the uncertainty in independently determining the metal film thickness (10%) and choosing the value for the imaginary part of the dielectric constant of the silver[24] (50%) at 1.06 μm. Using this range of parameter values, we found that the theoretical ratio can change by at least a factor of 10. For a reasonable choice of optical constants, which are those given in Table I, we fit the solid theoretical curve and the experiment points at the fundamental plasmon peak as shown in Fig. 2. This single normalization between the theoretical scale and the experimentally observed signals was used for the rest of the experiments reported here. As the signal levels change by over 4 orders of magnitude, great care was exercised in preserving this normalization when photomultiplier voltages and laser filters were changed.

An independent check of our calibration procedure was permitted by noting that in Fig. 2 in the plateau region of the curve at angles of incidence above θ_p the contribution to the SHG is due to the metal surface and not the crystal. The theoretical curve in this region is now determined by the result of Sipe's theory and is not nearly so sensitive to the choice of values for the optical parameters. The agreement with the observed signal level is excellent.

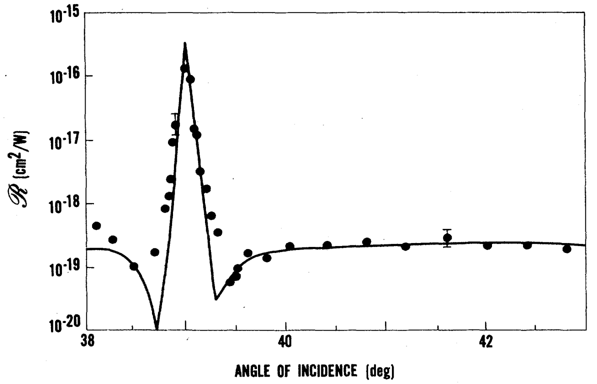

FIG. 2. Reflected SHG ($\mathscr{R}$) vs interior angle of incidence for rutile prism/550-Å-thick Ag film/X-cut quartz in standard experiment. Normalization to theoretical solid curve as discussed in text.

A. Ag on KDP

The first experiment was designed to demonstrate the additional enhancement in reflected SHG due to simultaneous fundamental SP excitation and quasi phase matching. Lee and Bloembergen[25] have shown that phase matching in total internal reflection may be realized if the condition $\theta_c(\omega)=\theta_c(2\omega)$ is achieved, where $\theta_c(\omega)$ and $\theta_c(2\omega)$ are the fundamental and the nonlinear harmonic critical angles, respectively. We achieve quasi phase matching by orienting a birefringent KDP crystal so that $\theta_P(\omega)=\theta_c(2\omega)$. A $10\times10\times5$ mm^3 KDP crystal obtained from Cleveland Crystal was cut so that the normal to the entrance face made an angle of $\phi=60°$ with respect to the crystal z axis while the crystal y axis was perpendicular to the plane of incidence as shown in the inset of Fig. 3. In this orientation of KDP a p-polarized fundamental produces an s-polarized P^{NLS} and we have

$$\tilde{P}_y^{\mathrm{NLS}}=2d_{14}^{\mathrm{KDP}}\sin(\theta_3-\phi)\cos(\theta_3-\phi)\ .$$

A 400-Å-thick silver film was evaporated on the polished crystal face and the crystal was optically contacted with bromonapthalene to a sapphire prism, chosen for the convenience of having the incident beam near normal incidence on the entrance prism face. The result of the experiment is shown by the solid dots in Fig. 3 where the reflected SHG ratio is plotted versus the internal angle in the vicinity of the fundamental plasmon angle. The solid

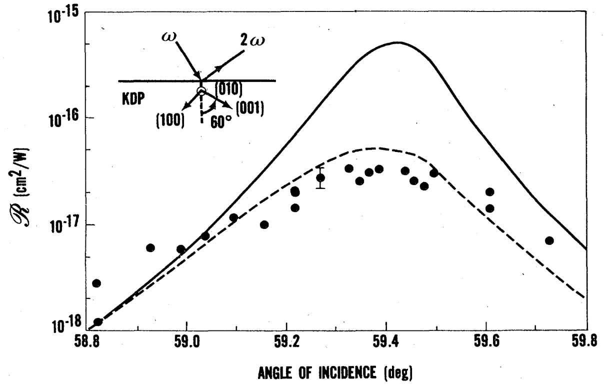

FIG. 3. Quasi-phase-matched reflected SHG ($\mathscr{R}$) vs interior angle of incidence for sapphire prism/440-Å-thick Ag film/KDP crystal oriented as shown in inset. Solid and dotted curves are theoretical calculations with unadjusted and adjusted Ag optical constants, respectively.

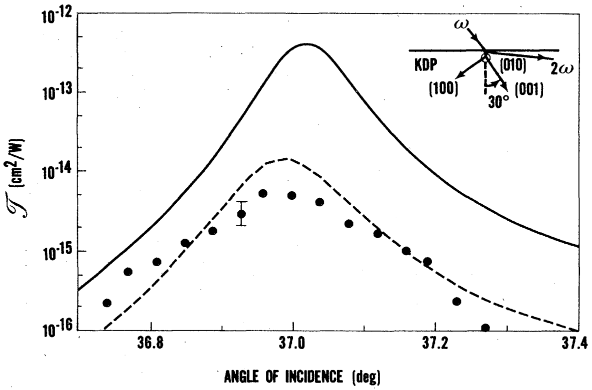

FIG. 4. Transmitted SHG ($\mathscr{T}$) vs interior angle of incidence for rutile prism/500-Å-thick Ag film/KDP crystal orientated as shown in inset. Solid and dotted curves are theoretical calculations with unadjusted and adjusted Ag optical constants, respectively.

theoretical curve is calculated using Eqs. (2)–(4) and (5b) with the optical constants given in Table I. The vertical scale for the experimental points on this curve is determined by comparing the signal level in this experiment to the signal level of the standard SP SHG experiment, which in turn had been calibrated to the theory through the Maker experiment as discussed before. By using this normalization procedure we see that although the predicted angular dependence of the SP resonance is observed, the absolute signal level of the resonance is an order of magnitude smaller than that predicted. Because KDP is a water-soluble crystal it is difficult to achieve the same smooth surface finish as can be achieved from crystal quartz. In addition, the prism-clamping procedure probably contributes to the roughening of the KDP surface. Repeated attempts at recoupling the KDP crystal produced similar results. If we account for the roughness of the KDP crystal/Ag interface by increasing the absorptive part of the Ag dielectric constant by a factor of 2, a new theoretical curve shown by the dotted lines in Fig. 3 is produced which fits the observed data.

A second experiment utilized the birefringence of KDP to permit a single evanescent-wave SP mode to drive a propagating harmonic wave. Here the requirement that the nonlinear harmonic critical angle $\theta_c(2\omega)$ be greater than the fundamental surface-plasmon angle $\theta_p(\omega)$ is achieved. Under these conditions the fundamental field in the nonlinear crystal is an evanescent field, as is the driven nonlinear polarization wave, which, however, can radiate a propagating harmonic wave. The KDP crystal, upon which a 500-Å-thick Ag film was evaporated, was orientated with the normal to the front face at an angle of $\phi = 30°$ with respect to the crystal Z axis and the crystal Y axis perpendicular to the plane of incidence as shown in the inset in Fig. 4. The 5 mm thickness of the crystal permitted a harmonic beam to be easily detected exiting from the polished side face of the crystal. The result of the experiment is shown by the solid dots in Fig. 4, where the transmitted SHG ratio is plotted on a logarithmic scale versus the internal angle of incidence. The transmitted SHG goes to zero at $\theta_c(2\omega) = 37.5°$. The normalization of the experimental data to the ordinate was accomplished following the procedure described previously. The solid theoretical curve is calculated using Eqs. (6)–(8) with $\tilde{P}_y^{\mathrm{NLS}}$ given for KDP as before. A large resonance is observed at the fundamental plasmon angle, but the actual observations are suppressed by almost 2 orders of magnitude in comparison to the theoretical level due to the relative softness of the Ag/KDP interface. The dotted curve is the theoretical result when the absorptive part of the silver dielectric constant is increased by a factor of 2 as before. Comparison of the two solid theoretical curves in Figs. 3 and 4 predicts that the SP-enhanced SHG in the transmission mode is close to 3 orders of magnitude greater than the SHG in the reflection mode. This factor results from the attenuation of the SHG propagating through the metal film in the reflection mode. The results of these two experiments where the observed ratio is over 2 orders of magnitude demonstrate this feature.

B. Al on quartz

The second set of experiments involved aluminum films evaporated on both X-cut- and Z-cut-quartz crystals. The motivation for these experiments was to attempt to reproduce the results reported by DeMartini *et al.*,[8] who claim to have observed both fundamental and nonlinear SP-excited reflected SHG from quartz crystals with thin Al films. In their first experiment a Z-cut-quartz crystal with the crystal X axis in the plane of incidence and the crystal Y axis perpendicular to the plane of incidence was used. (In this orientation the crystallographic and coordinate axes shown in Fig. 1 are identical.) For a p-polarized incident wave with this quartz orientation the nonlinear source term is $\tilde{P}_x^{\mathrm{NLS}} = d_{11}^{\mathrm{quartz}} \cos^2\theta_3$, where θ_3 is the transmitted angle for the fundamental wave in the nonlinear crystal. But at the fundamental critical angle $\cos\theta_3 \equiv 0$, while at the fundamental surface-plasmon angle this Z-cut-quartz projection factor produces a decrease in the SHG relative to the X-cut quartz of 10^{-4}. As a result, the SHG from the Z-cut quartz in this orientation is actually less than the surface SHG from the Al film. In their second experiment with the same Z-cut-quartz orientation the incident wave was s polarized and parallel to the crystal Y axis where now $\tilde{P}^{\mathrm{NLS}} = -d_{11}^{\mathrm{quartz}}$. No fundamental SP wave can be excited, but a harmonic SP wave may be theoretically calculated; however, due to the attenuation of the fundamental wave in the metal, the SHG resonance from the crystal is predicted to be at least 2 orders of magnitude smaller than that due to the metal. We further note that, for a 340-Å-thick Al film reported by DeMartini, a visible ATR resonance cannot easily be observed.

In our first experiment a 200-Å-thick Al film was evaporated on an X-cut-quartz crystal with the same orientation as used in the original Ag experiment where $P_z^{\mathrm{NLS}} = -d_{11}^{\mathrm{quartz}} \cos^2\theta_3$ and $\tilde{P}_x^{\mathrm{NLS}} = d_{11}^{\mathrm{quartz}} \sin^2\theta_3$ in the coordinate system of Fig. 1. The purpose of this experiment was simply to confirm that an Al film should produce SP-enhanced SHG comparable to a Ag film. The results of this experiment are shown by the solid points in Fig. 5, where the normalization of the data to the ordinate scale was done as described before and the theoretical curve is calculated with the optical constants given in Table I. The agreement of the data with the theory is excellent. Comparison of the SHG resonance on X-cut quartz with a 200-Å-thick Al film relative to that with a 500-Å-thick Ag film demonstrates that the peak of the resonance is actually a factor of 5 larger due to the relative thinness of the Al film; however, the angular width of the resonance is a factor of 5 broader due to the increased absorption of the Al relative to Ag in the near infrared.

Following DeMartini, we first evaporated a 340-Å-thick Al film on a Z-cut-quartz crystal. As expected, no resonant SHG due to the SP excitation was observed. In order to duplicate DeMartini's data (Fig. 5 of Ref. 8) we then repeated the experiment, but now with a 215-Å-thick Al film evaporated on the Z-cut-quartz crystal. The crystal X axis was in the plane of incidence and the incident radiation was p polarized. The results are shown by the solid dots in Fig. 6, where the reflected SHG ratio is now plotted on a linear scale but the data is still normalized as described before. A fundamental SP resonance in the SHG is clearly observed. However, when the aluminum-coated quartz crystal was replaced by a 200-Å-thick Al-coated fused-silica substrate, nearly identical results, shown by the open circles in Fig. 6, were achieved. The angular position of the fused-silica data was offset in Fig. 6 due to the difference in fundamental indices of refraction for crystal quartz and fused silica. The peaks of the two sets of data are equal to within the error bars. The solid theoretical curve was calculated using Sipe's free-electron theory for a 215-Å-thick Al film on a Z-cut-quartz crystal, but the contribution to the SHG from the crystal is 2 orders of magnitude smaller than that from the metal and is not shown on the linear scale. From these results we conclude that DeMartini's observations of reflected SHG with fundamental SP excitation are due only to the metal response and not the crystal.

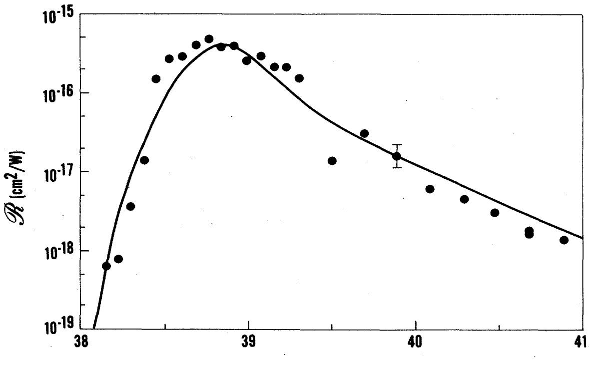

FIG. 5. Reflected SHG ($\mathcal{R}$) vs interior angle of incidence for rutile prism/200-Å-thick Al film/X-cut quartz.

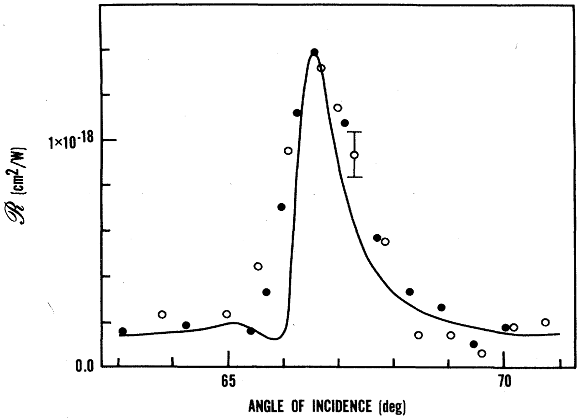

FIG. 6. Reflected SHG ($\mathcal{R}$) interior angle of incidence for SF-10 prism/215-Å-thick Al film/Z-cut-quartz crystal shown by solid circles and SF-10 prism/215-Å-thick Al film/fused-silica substrate shown by open circles. The solid curve is calculated from Sipe's theory for SHG from free-electron metals.

In the last experiment again with an aluminum film on a Z-cut-quartz sample oriented as before, the incident radiation was now s polarized and parallel to the crystal Y axis. As expected, no fundamental SP resonance was observed, but also no harmonic SP resonance was observed.[21] The theoretical SHG was calculated from Sipe's theory, but now including only the source term due to the bulk nonlinearity of the metal. Again, the SHG calculated from the crystal is 2 orders of magnitude smaller. A similar result was initially reported in our original investigation of SHG with Ag films on quartz crystals.[5] DeMartini claims that this latter result was due primarily to the high-index rutile prism used in our experiments. We have since investigated SHG in total internal reflection from opaque Ag and Al films deposited on a range of prisms from fused silica to rutile.[20] The results of these experiments are in excellent agreement with Sipe's theory which predicts no anomalous SHG for high-index prisms. In view of all these results we conclude that the peak in the SHG data shown in Fig. 6 of Ref. 8 cannot represent the nonlinear excitation of a SP mode.

C. Ag and Al on LiIO$_3$

The nonlinear excitation of the harmonic SP mode has been a major goal of this research. In the total-internal-reflection regime the fundamental field suffers exponential decay at all angles other than near the fundamental surface-plasmon angle, and thus the harmonic nonlinear polarization is strongly damped by several orders of magnitude. The competing effect of the SHG from the metal surface may be reduced but not eliminated by choosing the incident wave to be *s* polarized while using the nonlinear polarization tensor of the crystal to produce *p*-polarized SHG. Since our original attempt to observe this second SP resonance for a 500-Å-thick Ag film on an *X*-cut-quartz crystal failed, we chose for the nonlinear crystal *Z*-cut $LiIO_3$, which has a nonlinear susceptibility over an order of magnitude greater than that of quartz.[23] This experiment also failed to demonstrate the second SP resonance because the increased dispersion, and, hence, the reduced coherence length of the $LiIO_3$ crystal partially offset the enhancement due to the nonlinear susceptibility. But more significantly, the softness of the water-soluble crystal suppressed the enhancement due to the SP mode just as was the case in the KDP experiments.

To minimize the damping of the relatively thick 500-Å Ag film, a thin 100-Å Al film was then evaporated on a *Z*-cut $LiIO_3$ crystal. Although the SP resonance is inherently broader in Al than Ag, the thinner Al film permits more fundamental field to penetrate through to the nonlinear crystal. In addition, since the magnitude of the dielectric constant at the harmonic wavelength is larger in Al than Ag, the harmonic plasmon angle is closer to the harmonic critical angle in Al. This is particularly significant here because due to the large birefringence of $LiIO_3$ the harmonic plasmon angle actually occurs before the fundamental critical angle. The additional enhancement of reflection SHG due to the overlapping harmonic resonance structure associated with fundamental and harmonic critical angles is well known.[13] Although a broad resonance in the reflected SHG was finally observed in the vicinity of the harmonic SP resonance this structure could not be clearly resolved relative to the critical-angle structure.[21] We close this discussion by noting that the nonlinear excitation of the harmonic long-range surface-plasmon (LRSP) mode due to a thin 150-Å Ag film on an *X*-cut-quartz crystal was recently reported by us.[9]

IV. CONCLUSIONS

We have performed an extensive investigation of optical SHG from nonlinear piezoelectric crystals with simultaneous SP excitation. These experiments have emphasized not only the qualitative angular dependence associated with the SP resonance but also the quantitative aspects of the peak resonant phenomena. All the SP experiments reported here have been calibrated to a single Maker experiment. For a 500-Å-thick Ag film evaporated on an *X*-cut-quartz crystal the peak resonant SHG with fundamental SP excitation agrees with the theoretical calculation to within a factor of 2; however, the theoretical value can change by as much as an order of magnitude for a reasonable range of values of the imaginary part of the metal dielectric constant and metal-film thickness. By utilizing the birefringence of an appropriately oriented KDP crystal with an evaporated thin Ag film, SP-enhanced SHG is observed in reflection with quasi phase matching and in transmission through the polished side exit face of the crystal. The resonant SHG effects due to SP excitation with KDP crystals are reduced from the theoretical values by over an order of magnitude. This reduction is due to the apparent softness of the optically polished surface of the water-soluble KDP crystal. Although a linear ATR minimum was observed with these samples, the nonlinear SHG resonance is a more sensitive probe of the optical surface quality. The theoretical effect of the surface quality on the SP resonance can be obtained by arbitrarily doubling the absorptive part of the complex metal dielectric constant.

A series of experiments with aluminum films evaporated on orientated quartz crystals was performed. For a 200-Å-thick Al film on *X*-cut-quartz resonant SHG due to fundamental SP excitation was observed at a level of a factor of 5 greater than with a 500-Å-thick Ag film and was in good agreement with the calibration Maker experiment. When a 215-Å-thick Al film was evaporated on a *Z*-cut-quartz crystal the SHG due to the crystal was suppressed by over 2 orders of magnitude. In this case the fundamental SP produces an observable SHG resonance which is due only to the contribution from the metal surface. When the *Z*-cut-quartz crystal is replaced by a fused-silica substrate, a similar SHG resonance is observed. The level of the SHG in these experiments is consistent with the free-electron theory for SHG from metal surfaces. When incident *s* polarization is used in the same experiment we observe featureless low-level SHG, which is again in agreement with the results of Sipe's theory. The calculated resonance in the SHG due to the nonlinear excitation of the harmonic SP mode in the quartz crystal is 2 orders of magnitude smaller than the observed effect. We conclude that DeMartini's results for SHG with fundamental SP excitation are due only to metal-surface sources and not the nonlinear crystal and that the nonlinear excitation of the SP mode has not been demonstrated in these experiments.

A series of experiments using both Ag and Al films on *Z*-cut $LiIO_3$, which has a nonlinear susceptibility an order of magnitude greater than that of quartz, was performed in order to enhance the nonlinearly excited SP mode. For the thicker 500-Å Ag films the metal SHG still dominated the crystal SHG response. For the thinner 100-Å Al film the resonant structure in the reflected SHG in the vicinity of the fundamental and harmonic critical angles obscured the harmonic SP resonance which again was further suppressed due to the softness of the optical surface of the water-soluble $LiIO_3$ crystal. Observation of the harmonic SP mode using prism-coupling techniques with water-soluble crystals which have large nonlinear susceptibilities will be very difficult.

In conclusion we have demonstrated that the plane-wave theory of optical SHG with SP excitation from metal films on nonlinear crystals may be applied to a variety of metals and crystals to predict both the angular dependence and the intensity of these resonances.

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