Raman scattering of light by surface polaritons coherently excited on a rippled BeO crystal

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Raman scattering (RS) of light by nonuniform and surface polaritons (SPs), which were additionally illuminated by radiation from a frequency-tunable infrared (IR) laser, was studied experimentally. The experiments were conducted on a noncentrally symmetric BeO crystal whose surface was periodically rippled so that the incident IR radiation could excite SPs. The positions (localization curves) of the extrema in the k spectra of the RS and IR-reflection signals were determined as functions of the IR-illumination frequency. A k gap was observed in the locations of the maxima of the k spectra for RS of light by SPs in the region corresponding to intersection of the dispersion branches of the SPs at the edge of the reduced Brillouin zone. The method is also of interest for studying the influence of different types of disturbances of the interface between two media on the process by which photons are converted into SPs.

The nonlinear optics of surfaces has been attracting significant attention in the last few years. It is of interest both from the standpoint of clarifying the physical characteristics of nonlinear-optical processes in relation to their volume analogs and in the light of the development of new methods of diagnostics of surfaces and interfaces. Surface polaritons (SPs), propagating along an interface, are localized in a thin surface layer with a thickness on the order of a wavelength (see, for example, Refs. 1–2), and when involved in the interaction process, can play an important role in the nonlinear optics of surfaces.

This work is devoted to the experimental study of Raman scattering (RS) of light by SPs excited (with additional illumination) on a periodically perturbed (rippled) surface of a BeO crystal by IR-laser radiation. The process of Raman scattering of light by coherently excited SPs can also be regarded as a nonlinear-optical mixing (generation of the sum and difference frequencies) of body and surface waves in a medium with quadratic nonlinearity, when the incident IR radiation is converted into surface polaritons.[1)]

Surface polaritons can exist on a flat crystal-air boundary if the permittivity $\varepsilon(\omega)$ of the crystal is a negative quantity ($\varepsilon(\omega) < -1$). This condition is satisfied in the spectral range between the frequencies of longitudinal (LO) and transverse (TO) optical phonons. A BeO crystal was chosen as the object of investigation because the range of existence of SPs in this crystal overlaps with the lasing range of the CO_2 laser, whose radiation we employed for illuminating the SPs.

It is well known that an electromagnetic wave incident on the surface of a crystal whose dielectric permittivity is negative penetrates only to a depth less than or of the order of the wavelength, and it is partially absorbed and reflected back into the air (we shall call such nonpropagating mixed electromagnetic-mechanical excitations nonuniform polaritons, since they are genetically related to the volume polaritons but are essentially not quasiparticles). Nonuniform polaritons are formed virtually for any angles of incidence of the electromagnetic radiation, while surface polaritons cannot be excited by a smooth surface due to the fact that the energy and momentum conservation laws are not satisfied for the incident wave and the surface polaritons. The excitation of SPs becomes possible if the crystal surface contains "sources" of additional momentum. In our experiments we created a periodic structure (ripple)—which was the "source" of such additional momentum—on the surface of a BeO crystal in order to create the conditions for excitation of SPs. As a result, the IR radiation incident on the sample could excite both nonuniform and surface polaritons, which, generally speaking, must be manifested differently in the RS spectra (nonlinear-optical mixing).

2. SURFACE POLARITONS IN A BeO CRYSTAL

A uniaxial BeO crystal exhibits weak anisotropy and has a hexagonal structure of the wurtzite type (space group C_{6v}^4) with two formula units per unit cell. The nine optical excitations decompose as follows into irreducible representations: $A_1(z)+E_1(x,y)+2E_2+2B_1$. The RS and IR active excitations consist of a single excitation having the symmetry $A_1(z)$ and polarized along the z axis and a single doubly degenerate excitation having the symmetry $E_1(x,y)$ and polarized perpendicular to the z axis. The parameters of these excitations, which we measured from the spectra of spontaneous RS of light by optical phonons, are presented in Table I for the two samples which differ most from one another (the measurements showed that the phonon dampings vary somewhat from sample to sample). Some data on the phonon spectra of a BeO crystal are also contained in Refs. 18–20.

It is evident from Table I that the damping of the longitudinal and transverse optical phonons of a BeO crystal differ strongly in magnitude, i.e., the damping constant is a function of the frequency. This indicates that in this case the widely employed quasiharmonic approximation is not applicable for calculating the dispersion of the dielectric permittivity in the spectral range of interest to us. In

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TABLE I. Frequencies ν_{TO} and ν_{LO} and damping constants Γ_{TO} and Γ_{LO} of transverse and longitudinal, respectively, optical phonons with symmetry $A_1(z)$ and $E_1(x,y)$ in a BeO crystal (cm^{-1}).

$A_1(z)$				$E_1(x,y)$			
ν_{TO}	Γ_{TO}	ν_{LO}	Γ_{LO}	ν_{TO}	Γ_{TO}	ν_{LO}	Γ_{LO}
678	2,3	1078	16	723	1,2	1097	11,5
678	3	1078	16	723	1,8	1097	15

this connection, we employed the factorized Lidden–Sax-Taylor relation[21-23] in order to describe the dispersion of the dielectric permittivity (which determines the properties of polaritons) of a BeO crystal:

$$\varepsilon(\nu)=\varepsilon_\infty \frac{\nu_{LO}^2-\nu^2-1\nu\Gamma_{LO}}{\nu_{TO}^2-\nu^2-1\nu\Gamma_{TO}}, \tag{1}$$

which in the simplest model takes into account the dispersion of the damping constant and is applicable in the range between the frequencies ν_{LO} of longitudinal phonons and the frequencies ν_{TO} of the transverse optical phonons. Here ε_∞ is the dielectric permittivity of the crystal at frequencies significantly higher than ν_{TO}.

Since BeO is an anisotropic crystal, the dispersion of the surface polaritons depends, in the general case, on the direction of propagation and orientation of the crystal surface with respect to the crystallographic axes (see, for example, Refs. 1 and 2). In the experiments with surface polaritons we employed Z-cuts, i.e., the surface polaritons were excited on a surface oriented perpendicular to the optic axis Z of the crystal. In this case the dispersion of the surface polaritons is described by the following relation:

$$\frac{k_{sp}^2(\nu)}{(2\pi\nu)^2}=\frac{\varepsilon_\perp(\nu)-1}{\varepsilon_\parallel(\nu)\varepsilon_\perp(\nu)-1}\varepsilon_\parallel(\nu)=\varepsilon_{sp}(\nu). \tag{2}$$

Here $\varepsilon_\perp(\nu)$ is determined from the relation (1) by substituting into it the parameters of photons with $E_1(x,y)$ symmetry and $\varepsilon_\infty=\varepsilon_{\infty\perp}$, while $\varepsilon_\parallel(\nu)$ is determined by substituting the parameters of phonons with $A_1(z)$ symmetry and $\varepsilon_\infty=\varepsilon_{\infty\parallel}$. It is obvious that in the experimental geometry the dispersion of the SPs does not depend on the propagation direction in the plane of the crystal surface, i.e., such surface polaritons can be said to be ordinary.

From Eq. (2) we obtain for the real part k'_{sp} and imaginary part k''_{sp} of the wave vector of the surface polariton

$$k'_{sp}(\nu)=2\pi\nu\left[\frac{|\varepsilon_{sp}(\nu)|+\varepsilon'_{sp}(gn)}{2}\right]^{1/2},$$

$$k''_{sp}(\nu)=2\pi\nu\left[\frac{|\varepsilon_{sp}(\nu)|-\varepsilon'_{sp}(\nu)}{2}\right]^{1/2}, \tag{3}$$

where

$$\varepsilon'_{sp}=\{|\varepsilon_\parallel|^2(|\varepsilon_\perp|^2-\varepsilon'_\perp)-\varepsilon'_\parallel(\varepsilon'_\perp-1)+\varepsilon''_\perp\varepsilon''_\parallel\}/D,$$

$$\varepsilon''_{sp}=\{|\varepsilon_\parallel|^2\varepsilon''_\perp+\varepsilon''_\parallel-(\varepsilon'_\perp\varepsilon''_\parallel+\varepsilon''_\perp\varepsilon'_\parallel)\}/D, \tag{4}$$

$$D=(\varepsilon'_\perp\varepsilon''_\parallel-\varepsilon''_\perp\varepsilon''_\parallel-1)^2+(\varepsilon'_\perp\varepsilon''_\parallel+\varepsilon''_\perp\varepsilon'_\parallel)^2.$$

It is assumed that all permittivities in the relations (4) are functions of the frequency.

The corresponding relations for nonuniform polaritons, excited by an IR field at normal incidence on the surface of a Z-cut crystal, are described by the following relations:

$$k'_p(\nu)=2\pi\nu\left[\frac{|\varepsilon_\perp(\nu)|+\varepsilon'_\perp(\nu)}{2}\right]^{1/2},$$

$$k''_p(\nu)=2\pi\nu\left[\frac{|\varepsilon_\perp(\nu)|-\varepsilon'_\perp(\nu)}{2}\right]^{1/2}. \tag{5}$$

The results of the calculation of $k'_{sp}(\nu)$ and $k'_p(\nu)$, performed on the basis of the relations (1)–(5) using the data from the top row of the table and the values $\varepsilon_{\infty\perp}=2.95$ and $\varepsilon_{\infty\parallel}=2.99$, taken from Ref. 18, are shown in Fig. 1. The figure also shows the frequency dependence of the penetration depth of normally incident IR radiation

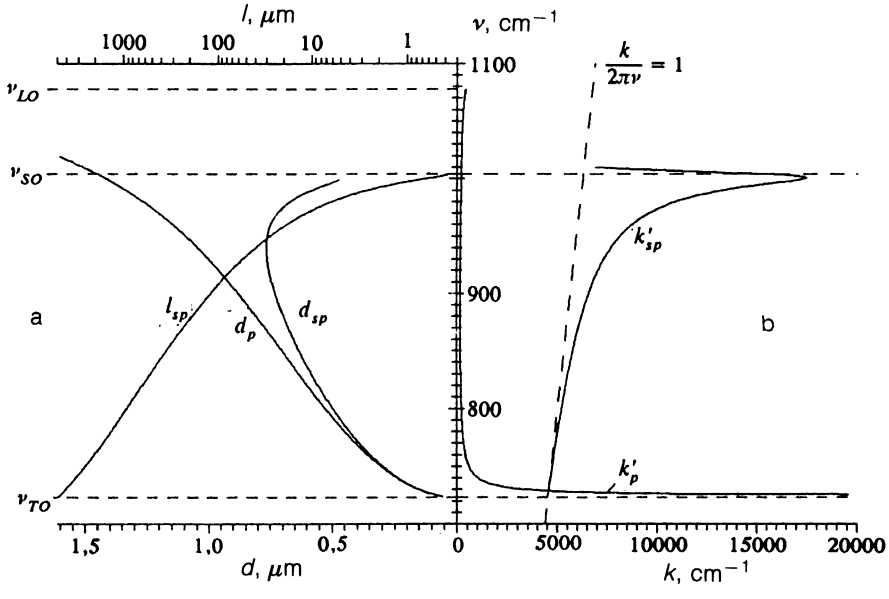

FIG. 1. a) Frequency dependences of the penetration depth $d_p(\nu)$ of normally incident IR radiation in the crystal and the mean free path $l_{sp}(\nu)$ and penetration depth $d_{sp}(\nu)$ of the surface polariton in the crystal; b) dispersion of the real parts of the wave vectors of nonuniform $k'_p(\nu)$ and surface $k'_{sp}(\nu)$ polaritons. Here ν_{SO} is the frequency of surface optical phonons, ν_{TO} is the frequency of transverse optical phonons with symmetry $E_1(x,y)$, and ν_{LO} is the frequency of longitudinal optical phonons with symmetry $A_1(z)$.

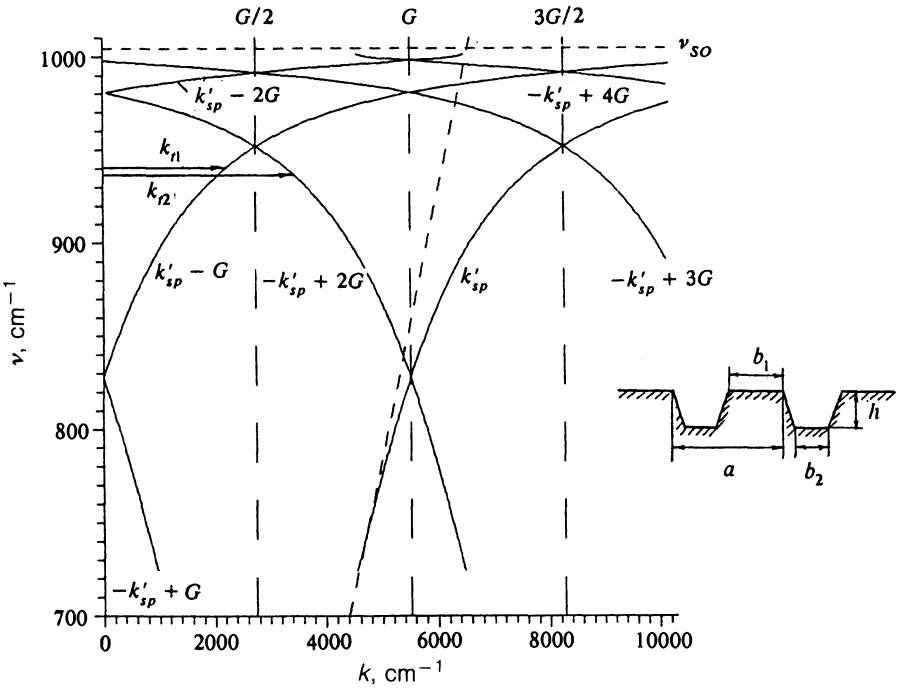

FIG. 2. Sample, calculated using Eq. (7), of the dispersion curves of surface polaritons on a periodically perturbed (with period $a=11.4$ μm) BeO crystal surface oriented perpendicular to the optic axis. The dashed line $k=2\pi\nu$ corresponds to dispersion of photons in vacuum; k_{t1} and k_{t2} are the projections of the wave vector of IR radiation incident on the grating for which excitation of surface polaritons at fixed frequencies is possible. $G=2\pi/a$ is the reciprocal lattice vector. Inset: average profile of the grating prepared on the surface of a BeO crystal: $a=11.4$ μm; $b_1=6.8$ μm; $b_2=2.1$ μm; $h=0.24$ μm.

in the crystal, $d_p(\nu) = 1/k''_p(\nu)$, as well as the mean free path of surface polaritons along the surface, $l_{sp}(\nu) = 1/2k''_{sp}(\nu)$, and the penetration depths of the surface polariton field into the crystal $d_{sp}(\nu) = 1/k'_n(\nu)$, where

$$k_n(\nu)=k'_n(\nu)+ik''_n(\nu)=\frac{1}{2\pi\nu}\left[\varepsilon_\perp^2\,\frac{1-\varepsilon_\parallel}{\varepsilon_\parallel\,\varepsilon_\perp-1}\right]^{1/2}. \quad (6)$$

The penetration depths actually determine the volumes of the nonlinear-optical interaction of the probe and IR radiation in the crystal when nonuniform and surface polaritons are excited.

It is evident from Fig. 1 that over the entire range of existence of surface polaritons the wave vector k'_{sp} is greater than the wave vector of photons in air ($k=\omega/c$). This means that the IR radiation incident on the crystal surface cannot excite surface polaritons. In order to excite surface polaritons by external IR radiation (in order for the wave vectors to match) a periodic structure (grating), whose average parameters were determined with the help of an MII-4 interference microscope and are displayed in the inset in Fig. 2, was produced on the surface of the BeO crystal by a photolithographic method.

In the case when a surface polariton propagates perpendicular to the lines of the grating the dispersion relation (3), which holds for a flat surface, is modified and, to a first approximation (neglecting interaction of SPs excited in different orders of diffraction), acquires the following form:

$$k_m^{\pm}=\pm k'_{sp}+mG, \quad (7)$$

where $m=0, \pm1, \pm2,...$; $G=2\pi/a$ is the reciprocal lattice vector of a structure with period a. Thus the k space is covered with m dispersion curves, separated by a distance G, and these curves can intersect one another. A sample of such curves, which is of interest for further analysis and was calculated using the relations (3) and (7) for a BeO crystal with $a=11.4$ μm, is presented in Fig. 2.

The condition for excitation of surface polaritons by IR radiation incident on the crystal surface at an angle θ with respect to the normal to the surface (the plane of incidence is perpendicular to the grating lines and the IR radiation is polarized in the plane of incidence) is now determined by the following relation:

$$k_t \equiv k_{IR}\sin\theta = k_m^{\pm}, \quad (8)$$

where k_t is the projection of the wave vector of the IR radiation $k_{IR}=2\pi\nu_{IR}$ on the crystal surface. It follows from the relation (8) and Fig. 2 that surface polaritons whose dispersion branches fall into the interval between the ordinate and the "photon" line ($k=2\pi\nu$) can be excited by means of IR radiation. In the range of interest to us (925–980 cm^{-1}) these are $k_{-1}^{+} = k'_{sp} - G$ and $k_{+2}^{-} = -k'_{sp} + 2G$, which can be excited for angles of incidence θ_1 and θ_2 determined from the conditions

$$k_{t1}=k_{IR}\sin\theta_1=k'_{sp}-G,$$

$$k_{t2}=k_{IR}\sin\theta_2=-k'_{sp}+2G. \quad (9)$$

At these angles the reflection of IR radiation from the rippled surface of a BeO crystal should decrease as a result of excitation of SPs, and the dependence of the reflected signal on the angle of incidence (projection of the wave vector on the surface) corresponds to the spectrum of SPs in k space, i.e., the position of the reflection minimum is determined by the real part of the wave vector k'_{sp} of the polariton and the angular width of the "dip" in the reflected signal is determined by the imaginary part, i.e., k''_{sp}.

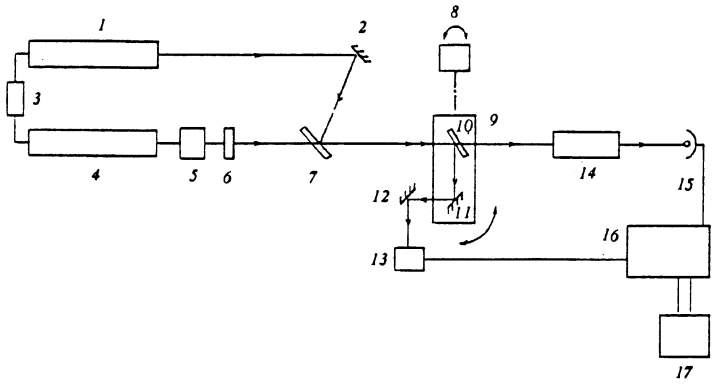

FIG. 3. Schematic diagram of the experimental apparatus: *1*—frequency-tunable CO_2 laser; *2*—mirror; *3*—unit synchronizing the lasing pulses of CO_2 and Nd YAG lasers (4); *5*—Nd YAG laser frequency doubler; *6*—light filter, transmitting the second-harmonic ($\lambda_1=0.532$ μm) and absorbing the radiation of Nd YAG laser; *7*—dichroic mirror; *8*—stepping motor, rotating the platform (*9*) with the experimental crystal (*10*) and the mirror (*11*), reflecting the IR radiation; *12*—mirror; *13*—IR detector; *14*—monochromator and light filter, separating the scattered light; *15*—photomultiplier; *16*—two-channel pulse amplitude averager (boxcar); *17*—$X-Y$ automatic plotter.

3. EXPERIMENTAL PROCEDURE

The RS of light by coherently excited polaritons was investigated experimentally on the apparatus shown schematically in Fig. 3. The polaritons were excited by discretely frequency-tunable (in the range $\approx$920–1080 cm^{-1}) radiation from a transversely excited atmospheric-pressure periodic-pulse CO_2 laser (TEA laser) (1) with pulse repetition frequency up to 10 Hz. A typical pulse from this laser consists of a short spike with a duration of the order of 150 nsec and a "tail" extending in time up to approximately 1 μsec. The energy in the spike was 25–50% of the total energy in a pulse, equal to 10 mJ (the energy depends on the lasing frequency, and the value presented corresponds to the maximum value).

After reflecting from a dichroic mirror (*7*) the CO_2-laser radiation strikes the rippled surface of the experimental sample (*10*), consisting of a BeO-crystal plate approximately 1 mm thick. The radiation was polarized in the plane of incidence, oriented perpendicular to the lines of the periodic structure. The radiation reflected from the rippled surface in zeroth diffraction order was directed with the help of the mirrors (*11*) and (*12*) onto the photodetector (*13*), the signal from which was fed, after averaging, to an X-Y automatic plotter (*17*). The excitation of the SPs was monitored by means of the dependence of the reflected signal on the angle of incidence θ—when the condition (*18*) is satisfied, the reflected signal should decrease in strength, which would indicate that the incident IR radiation had been converted into a surface polariton. The angle of incidence was changed by rotating the table (*9*) with the help of a stepping motor (*8*). We note that a mirror (*11*), oriented at an angle of 90° with respect to the "working" surface of the crystal (*10*), was placed together with the crystal on the rotating table (*9*). With this scheme, as the angle of incidence changes the beam reflected from the mirror (*11*) is displaced in a parallel direction; this makes it possible to eliminate displacement of the beam along the photodetector (*13*), if the detector is placed in the focal plane of a converging lens.

The probe beam consisted of the second-harmonic radiation of a periodic-pulse Nd YAG laser (*4*) (the wavelength of the probe radiation was $\lambda_L=0.532$ μm, and the pulse energy reached 10 mJ with pulse length of about 10 nsec). The CO_2- and YAG-laser pulses were synchronized in time, and these laser beams were merged with the help of the dichroic mirror (*7*). The probe beam and the IR radiation were polarized in the plane of incidence, oriented perpendicular to the grating lines.

The Stokes component of the probe beam Raman-scattered by IR-excited polaritons was recorded in the forward direction at small angles with respect to the probe and IR radiation. The scattered light was separated from the probe beam with the help of an interference light filter and a monochromator (*14*) and recorded with the help of an FÉU-79 photomultiplier (*15*), the signal from which was averaged and fed into an X-Y automatic plotter (*17*).

Thus the experimental procedure enables the amplitudes of both the IR radiation reflected from the surface of the experimental sample and the scattered signal to be recorded simultaneously as functions of the angle of incidence of the collinearly propating probe and IR beams.

4. RESULTS AND DISCUSSION

The interaction of the probe and IR radiation incident on the crystal results, under the conditions described above, first, in Raman scattering by nonuniform polaritons, which are excited by the IR radiation at any angles of incidence. The light scattered by nonuniform polaritons propagates practically along the probe beam. Moreover, at certain angles of incidence, determined by the condition (*8*), surface polaritons propagating along the surface should be excited and scatter the probe beam. It follows from Eq. (9) that surface polaritons excited in different orders of diffraction should propagate in opposite directions. This results in different scattering angles (see Fig. 4), whose values can be calculated from the conservation of energy and tangential components of the wave vectors for an elementary event of Raman scattering by a surface polariton:

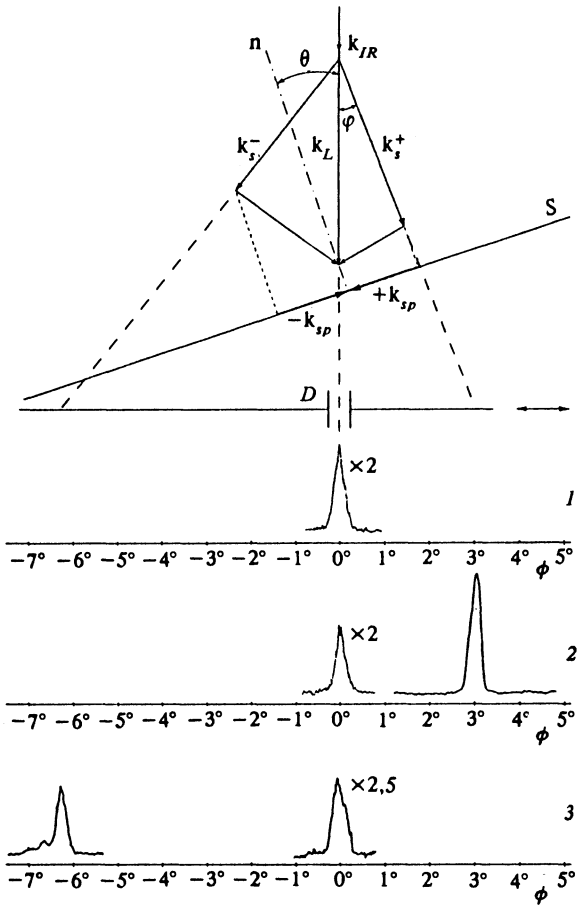

FIG. 4. Relative arrangement of the wave vectors of the interacting waves with Raman scattering of light by surface polaritons propagating in the opposite directions $+k_{sp}$ and $-k_{sp}$; *S*—surface of the crystal; *D*—diaphragm. Bottom: scattered signal versus the scattering angle φ; the curves were obtained by scanning a 3 mm in diameter diaphragm *D* in a direction perpendicular to the probe beam with $\nu_{IR}=944.2$ cm^{-1} and different angles θ of incidence of collinearly propagating probe and IR beams on the grating: $\theta=20°$ (*1*), 28.7° (*2*), and 27.1° (*3*).

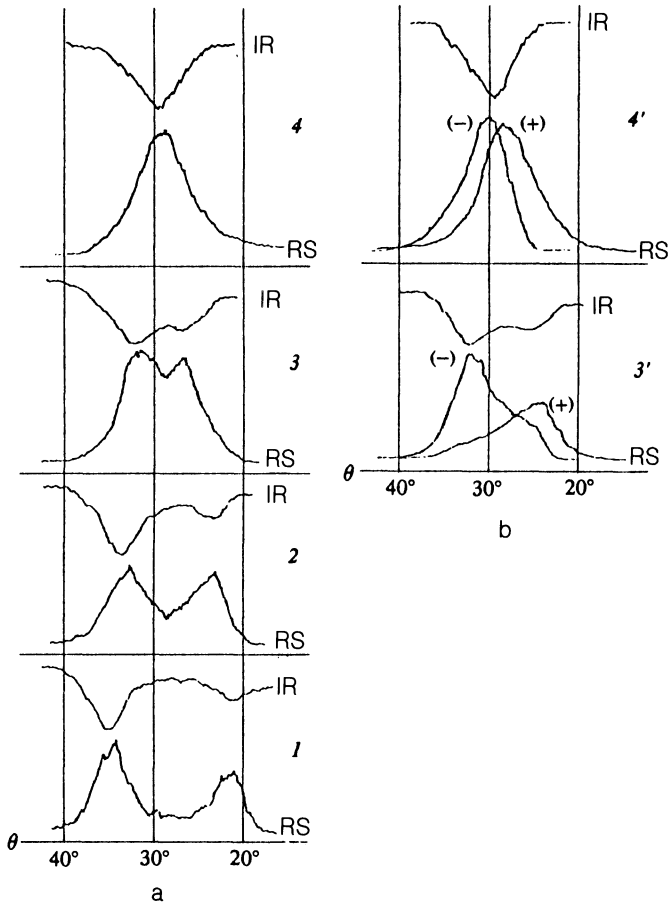

FIG. 5. a) Experimental curves of the scattered signal (RS) and IR-reflection signal (IR) as a function of the angle of incidence θ on the grating. The curves were obtained for different fixed values of ν_{IR}: 931.0 (*1*), 934.9 (*2*), 938.7 (*3*), and 944.2 cm^{-1} (*4*). b) The curves (*3'*) and (*4'*) are analogous to the curves (*3*) and (*4*), respectively, except that they were obtained with separate recording of the signal corresponding to Raman scattering by surface polaritons belonging to different dispersion branches $k'_{sp}-G(+)$ and $2G-k'_{sp}(-)$.

$$k_L \sin\theta_1 = k_s \sin(\theta_1-\varphi_1)+k'_{sp},$$
$$k_L \sin\theta_2 = k_s \sin(\theta_2-\varphi_2)-k'_{sp}. \qquad (10)$$

Here k_L and k_s are the wave vectors of the probe and scattered light, respectively, and φ_1 and φ_2 are the scattering angles (the angles between $\mathbf{k}_L$ and $\mathbf{k}_s$) while θ_1 and θ_2 are determined by Eq. (9).

Thus Raman scattering of light by nonuniform polaritons as well as by surface polaritons, excited in different orders of diffraction, should occur in different directions with respect to the probe beam. This enables the signals arising due to the participation of different polaritons in the Raman scattering process to be recorded separately. In order to verify this we obtained the experimental dependence of the scattering signal on the scattering angle φ by moving the diaphragm *D* in a direction perpendicular to the probe beam (see Fig. 4) with IR illumination frequency $\nu_{IR}=944.2$ cm^{-1} and three fixed values of the angle of incidence θ of collinearly propagating probe and IR beams. It is evident that the Raman scattering of light by nonuniform polaritons is indeed observed along the probe beam for any angle of incidence (peaks with $\varphi=0°$ are present in all three curves). The Raman scattering of light by surface polaritons is observed only at resonance angles of incidence $\theta=28.7°$ and 27.1° (the curves (*2*) and (*3*) in Fig. 4) and scattering at these two angles occurs in different directions with respect to the probe beam. This indicates that surface polaritons excited in two different orders of diffraction propagate in opposite directions.

Next we measured the RS and IR-reflection signals as a function of the angle of incidence θ (k spectra) for different fixed IR illumination frequencies. The curves were recorded simultaneously with the help of an *X-Y* automatic plotter, and some of these curves are displayed in Fig. 5. When these spectra were recorded, a small screen was inserted in the path of the probe beam behind the experimental sample in order to eliminate the θ-independent signal corresponding to Raman scattering by nonuniform polaritons, and the scattered light was collected with the help of a wide-angle objective, simulta-

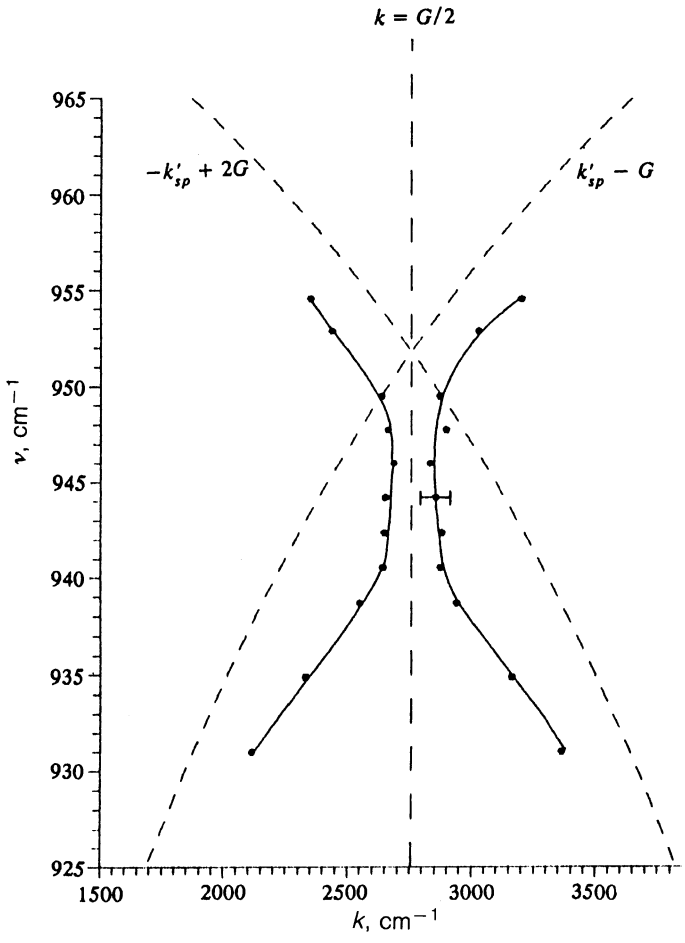

FIG. 6. Experimentally obtained localization curves of the maxima of the k spectra of Raman scattering of light by coherently excited surface polaritons (dots; the solid curves were drawn through the experimental points). The dashed curves were obtained by calculating the dispersion branches of surface polaritons $k_{-1}^{+} = k'_{sp} - G$ and $k_2^- = -k'_{sp} + 2G$.

neously "capturing" the Raman scattering by surface polaritons excited in two orders of diffraction.

It is evident from Fig. 5a that two minima and two maxima, corresponding to excitation of surface polaritons in two orders of diffraction, are correspondingly observed in the k spectra of both IR reflection and the RS signal, which were obtained at low IR-illumination frequencies (931, 934.9, and 938.7 cm^{-1} [see the spectra (1), (2), and (3)]. The angular positions of the minima in the IR spectra are identical to the positions of the maxima in the RS spectra. As the IR illumination frequency is increased, the angular separation between the extrema in the IR and RS spectra decreases, and for $\nu_{IR} > 939$ cm^{-1} they become indistinguishable. For $\nu_{IR} > 950$ cm^{-1} two extrema are observed once again (these spectra are not displayed in Fig. 5), and the separation between them increases with frequency. This behavior also follows qualitatively from Fig. 2.

In order to resolve the overlapping RS profiles in the range 939–950 cm^{-1} we employed this possibility of separately recording the spectra of Raman scattering by surface polaritons excited in different orders of diffraction. For these purposes the IR-reflection spectrum and the RS signal spectrum were recorded twice for two positions of the diaphragm (in accordance with Fig. 4), selecting the signals corresponding to scattering by surface polaritons of the two dispersion branches. Next the IR-reflection spectra were combined and we obtained two independent contours describing the Raman scattering of light by surface polaritons. These contours made it possible to determine the position of their maxima, which is impossible to do from the IR-reflection spectra. The result of this procedure, performed with $\nu_{IR} = 938.7$ and 944.2 cm^{-1}, is displayed in Fig. 5b, which demonstrates clearly that it is possible to separate overlapping RS spectra, corresponding to scattering by surface polaritons belonging to different dispersion branches [compare the spectra (3) with (3′) and (4) with (4′)].

The positions of the maxima of the k-spectra of Raman scattering of light by coherently excited surface polaritons in the $\omega - k$ plane, which were obtained from spectra, some of which are shown in Fig. 5, are displayed in Fig. 6. The dashed curves also show the dispersion of the surface polaritons, as calculated from Eq. (7). It is evident from Fig. 6 that the experimentally obtained curves are frequency-shifted as a whole by approximately 7 cm^{-1} with respect to the calculated dispersion curves of the surface polaritons. It can be conjectured that the observed shift is caused by the influence of etching, employed in fabricating the grating, on the optical properties of BeO and the fine-scale surface roughness, which is always present.

An interesting feature of the experimental curves of the position of maxima of the k-spectra of light Raman-scattered by coherently excited surface polaritons is the occurrence of a k gap (a gap in k space) in the vicinity of the intersection of the dispersion curves of surface polari-

tons with the wave vectors $k'_{sp} - G$ and $-k'_{sp} + 2G$ with $k = G/2$. A gap is not observed in the IR reflection spectra, and could be recorded in the RS spectra only because the signals corresponding to scattering by surface polaritons from different dispersion branches (see, for example, the spectrum (4′ in Fig. 5b), were recorded separately. The intersection of the dispersion curves corresponds to degeneracy of the states of two surface polaritons propagating in opposite directions. The interaction of the surface polariton through the grating results in a removal of degeneracy, i.e., anticrossing of the dispersion curves and the appearance, generally speaking, of an energy gap (ω gap).

It should be noted that the interaction of surface polaritons on the grating in the vicinity of the intersection of the dispersion branches has been studied many times experimentally using different methods for exciting the surface polaritons (see Refs. 1 and 2 and the references presented there). Here the extremal case, when a k gap and not an ω gap was observed in the frequency-angle distribution of the radiation when surface polaritons propagate along the grating, turned out to be somewhat unusual at first glance. This resulted in further elaboration of the theory and analysis of the corresponding spectra.[25–28] In these works, in particular, it is shown that the form of the localization curves of the minima in the reflection spectra and maxima in the emission spectra in the region of resonant interaction of surface polaritons can differ from the dispersion of surface polaritons and depends on the parameters of the grating, the properties of the surface polaritons and the method used for recording the corresponding spectra, i.e., using ω or k spectroscopy. The conditions under which k gaps can appear in the localization curves of the minima in the reflection spectra from metal gratings are discussed in Ref. 27 on the basis of model calculations.

Thus, in order to calculate the localization curves of any spectrum the complete problem of the response of the system to external fields must be solved in application to a specific experimental method. Next, the extrema of the complete response function must be determined; it is not enough to find the poles, which determine the dispersion of surface polaritons whose form can, generally speaking, be different from that of the localization curves of the extrema.[2)] Calculations performed thus far[1,2,25–28] are valid only for simple experiments.

5. CONCLUSIONS

We have investigated experimentally the basic features and laws of Raman scattering of light by coherently excited nonuniform and surface polaritons, excited on a periodically perturbed surface of a noncentrally symmetric BeO crystal. We studied the k spectra of Raman scattering and infrared reflection for different fixed frequencies of IR illumination and recorded separately three Raman scattering signals (with fixed IR illumination frequency), corresponding to scattering by nonuniform polaritons and surface polaritons from two different dispersion branches.

We obtained the positions of the maxima of the k spectra of RS signals and the IR-reflection minima. Independent recording of the spectra of Raman scattering by surface polaritons from different branches revealed a k gap in the localization curves of the maxima of the k spectra of Raman scattering near the edge of the Brillouin zone. A k gap is not observed in the curves of the position of the IR-reflection minima. A qualitative interpretation of the observed features was given. Further elaboration of the theory is required in order to give a quantitative description.

In conclusion we note that the method implemented in this work is also of interest for investigations of the influence of different types of surface "perturbations" (roughness, adsorbed resonately absorbing molecules, etc.) on the processes of transformation of photons into surface polaritons on the surface of noncentrally symmetric crystals. The signal corresponding to Raman scattering by nonuniform surface polaritons can be used as an internal measure of the conversion efficiency, since its amplitude is virtually independent of the state of the surface.

We thank V. A. Maslov for providing the BeO single crystals and the members of V. A. Sychugov's group for preparing the periodic surface structure.

[1)]Nonlinear-optical mixing spectroscopy of visible and IR radiation is now actively employed for studying volume polaritons[3–8] and thin molecular layers on an interface;[9–14] experiments displaying significant selective amplification of the RS signal with IR illumination of surface polaritons excited using the method of frustrated total internal reflection[8,15–17] have also been performed.

[2)]Another example is spontaneous Raman scattering of light by internal polaritons. Analysis[29–32] shows that the locations of the maxima of the spontaneous Raman scattering spectra generally speaking are different from the dispersion curves of polaritons (normal waves) in the vicinity of phonon resonances and the region where the electronic and lattice contributions to the quadratic nonlinear susceptibility cancel.

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