Fermi resonance of polaritons with bound and dissociated phonon states

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Using the method of Raman scattering at small angles, we report an experimental observation of polariton Fermi resonance produced as a result of crossing the polariton branch in the region of dissociated and bound states of two optical phonons in HIO_3 crystal.

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A polariton Fermi resonance is produced when the polariton branch crosses the frequency region of harmonics or composite tones of the fundamental oscillations of a crystal. In contrast to the isolated molecules, broad bands—bands of two-particle (dissociated) states, which are due to translational symmetry—rather than narrow lines, are generally produced in crystals in the region of harmonics and composite tones (second-order spectra). Moreover, when the anharmonicity in the region of the second-order spectrum is sufficiently strong, the bound or quasi-bound states (biphonons) can be produced in addition to the bands of two-particle states.[1,2] The behavior of the spectra of Raman scattering of light (RSL) by polaritons, under the conditions of the Fermi resonance with the bound states differs greatly from that with the dissociated state. Thus, for example, it follows from the theory developed in Ref. 3 that a Fermi resonance with the bound states produces an energy gap (discontinuity) in the dispersion branch of polaritons, and the dispersion of polaritons in the region of the bound state behaves in the same way as that in a resonance with fundamental oscillation, the only difference being that the oscillator strength of the bound state is determined by the anharmonicity. In the band of two-particle states the polariton dispersion, which can have a nonmonotonic nature, should be broadened because of the "inclusion" of an additional path for the decay of polaritons into two free phonons.

The experimental observation of certain aspects of the Fermi resonance of polaritons with bands of two-particle states was reported earlier (see Ref. 4 and the references therein). However, a case in which the polariton Fermi resonance occurs when a bound state is split off from the band of the two-particle states, and the polaritons interact with the dissociated and bound states of two phonons heretofore could not be observed experimentally. In this paper we report the first experimental observation of the Fermi resonance of this type, which was observed in the RSL spectra of polaritons.

The experiments were performed by using a double-axis HIO_3 crystal (point symmetry group 222). The first-order phonon spectrum for this crystal, which is fully referenced, may be broken down into four groups[5,6]: 1) lattice vibrations (0 –220 cm^{-1}); 2) deformation vibrations of the IO_3 group (290–400 cm^{-1}); 3) valence vibrations of the IO_3 group (600–845 cm^{-1}); 4) vibrations of the OH group: nonplanar deformation (torsional) vibrations (~ 560 cm^{-1}), planar deformation vibrations (~ 1160 cm^{-1}), and valence vibrations (~ 2940 cm^{-1}). Thus, in the frequency region of the phonons with $\nu > 1160$ cm^{-1} only one first-order line with $\nu \approx 2940$ cm^{-1} should be observed in the scattering spectra in each type of symmetry of the vibrations [$B(x)$, $B(y)$, $B(z)$, and A]. A detailed study of RSL using optical phonons in this region of the spectrum showed that at the low-frequency end of the oscillation with $\nu \approx 2940$ cm^{-1} a broad band is observed in the range to ~ 2270 cm^{-1}. A rather narrow line with $\nu = 2270$ cm^{-1}, whose intensity is comparable to that of the first-order line with $\nu \approx 2940$ cm^{-1}, [7] is also observed in the spectra for the scattering by polar optical phonons at the low-frequency end of this band. Figure 1 shows a part of the RSL spectrum for the optical phonons of symmetry $B(z)$ (the scattering was recorded at an angle of 90° relative to the propagation of the pump radiation), which illustrates the peculiarities described above. The band between the first-order 2940-cm^{-1} line and the 2270-cm^{-1} line corresponds to the scattering of light by the two-particle states, and the 2270-cm^{-1} line corresponds to the bound state.[7] These states were produced in the region of the harmonic oscillation with $\nu = 1160$ cm^{-1}.

This can be accomplished in the HIO_3 crystal by satisfying the following conditions. First, the oscillations of the OH group have the strongest anharmonicity, which

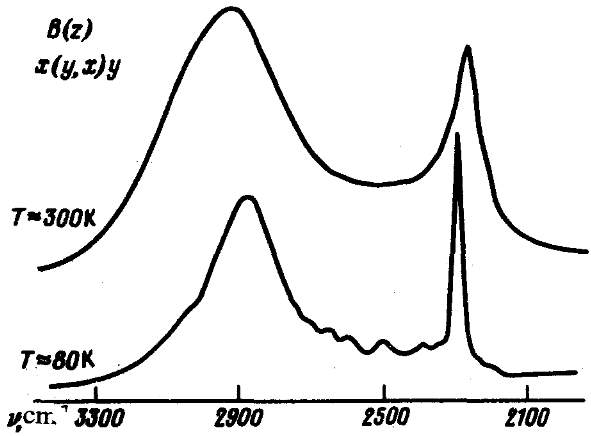

FIG. 1. Parts of the spectra for RSL by the optical phonons of $B(z)$ symmetry, which were obtained at sample temperatures of 300 K and 80 K. The scattering geometry is $x(y,x)y$; ν is the Stokes shift of the scattered radiation.

increases the probability for formation of bound the states in the region of the harmonic oscillations of this group. Second, in this case there is an especially strong Fermi resonance of the 2940-cm^{-1} oscillation with a 1160-cm^{-1} harmonic oscillation, which, according to Ref. 3, also contributes significantly to the formation of the bound states. The strong Fermi resonance in this case is due to the strong anharmonicity of the oscillations of the OH group and due to the fact that the fundamental tone ($\nu = 2940$ cm^{-1}) and the oscillation, which produces the resonant harmonic (2×1160 cm^{-1}), are excitations of the same OH group.

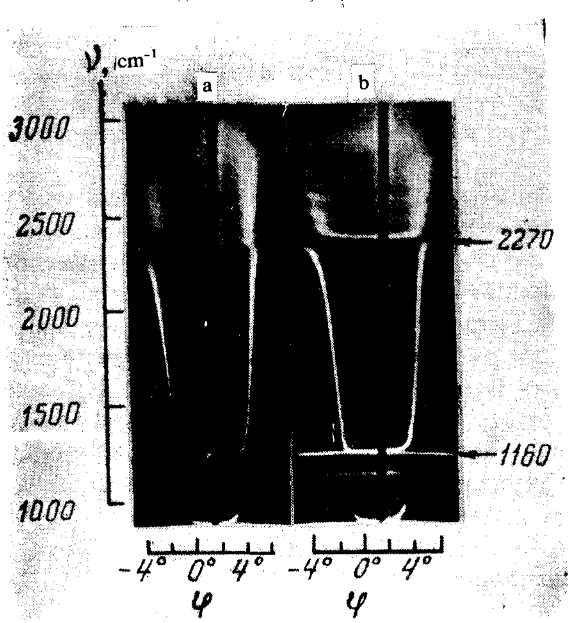

FIG. 2. Parts of the spectra for RSL by the polaritons of mixed symmetry $B(x)+B(z)$, which were obtained at sample temperatures of 300 K(a) and 80 K (b). ϕ is the scattering angle inside the crystal.

The study of RSL using polaritons was carried out by the method of scattering at small angles and by means of photography[4] in conjunction with the ISP-51 spectrograph; scattering was induced by an argon laser operating at the wavelength of 5145 Å. Moreover, a frequency-angle spectrum of RSL with polaritons was obtained directly on film, i.e., the dependence of the frequency of scattered light ν_s (or of polaritons ν) on the angle ϕ between the directions of the incident and scattered light. The pump radiation was propagated and was polarized in the xz-crystallographic plane. The recorded scattered radiation was also propagated in the xz plane and was polarized along the y axis. The angle between the direction of propagation of the incident radiation and the z axis of the crystal was 45°. This scattering geometry was chosen to satisfy the conditions for synchronism in order to observe the polaritons in the spectrum region of interest to us.

Figure 2 shows the frequency-angular spectra of RSL by polaritons of the HIO_3 crystal, which were obtained for the scattering geometry indicated above. It can be seen in the spectrum of Fig. 2a that in the frequency region of the bound state (2270 cm^{-1}) the polariton branch has a discontinuity (splitting) and in the band of the dissociated states it is greatly broadened. In addition, a significant redistribution of the intensity of scattering by polaritons, by dissociated states and by the bound states can be observed. The observed behavior of the scattering spectra is in good agreement with the theory developed in Ref. 3. The asymmetry of the frequency-angle spectra in Fig. 2 is attributed to the fact that the scattering is done by the mixed $B(z) + B(x)$ polaritons. It follows from these spectra that the oscillator strength of the biphonon of $B(z)$ symmetry is greater than the oscillator strength of the biphonon of $B(x)$ symmetry, since the splitting of the polariton branch near the biphonon in the region of positive scattering angles is smaller than that in the region of negative angles. It should also be noted that the biphonons of $B(x)$ symmetry can be clearly identified only by cooling the crystal.[7] Because of this, a sharp discontinuity of the polariton branch cannot be observed in the sample at room temperature in the region of positive scattering angles.

By cooling the crystal to a temperature of 80 K, the line width of the bound state (Fig. 1) decreases much more than that of the first-order line (2940 cm^{-1}), which is due to a decrease in the probability of dissociation of the biphonon into two free phonons. In addition, a structure (Fig. 1), which breaks the polariton branch (Fig. 2b) in the band, is formed in the band of the two-particle states as a result of cooling the crystal. The reason for the occurrence of such structure is not clear. It may be due to the critical points in the density of states, due to the formation of quasi-bound states in the band, or due to the interference of the two- and three-particle excitations. However, additional studies are needed to determine unambiguously the reason for the occurrence of such structure in the band of two-particle states as a result of cooling the crystal.

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