Angular characteristics of Raman scattering of light by a bound two-phonon state under conditions of polariton Fermi resonance in gallium-phosphide crystal

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Raman scattering (RS) of light is used to investigate the bound (biphonon) state under conditions of Fermi resonance with the fundamental polariton in a GaP crystal. The angular dependences of the frequency and of the intensity of RS by hybrid biphonon-polariton excitations are investigated experimentally. Satisfactory agreement between experiment and theory is obtained.

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1. INTRODUCTION

Accidental proximity of a phonon energy level to an energy band of two-phonon states of like symmetry can alter substantially the vibrational spectrum of a crystal lattice. The resonant interaction of the single- and two-particle excitations (Fermi resonance) which occurs under these conditions can lead to the appearance of bound phonon pairs (biphonons).[1,2] A characteristic feature of the conditions under which a biphonon is produced is strong anharmonicity of the lattice vibrations. In the case when the anharmonicity energy is large enough and exceeds the width of the energy band of the two-particle states, the biphonon energy level is produced outside this band.[2]

In noncentrosymmetric crystals, the Fermi resonance has certain singularities. In such crystals, the fundamental optical transverse optical (TO) lattice vibrations with wave vectors $k < 10^4$ cm^{-1} constitute hybrid photon-phonon excitations–polaritons. A characteristic property of a polariton is the strong dependence of the frequency ω on the wave vector k. As a result, the dispersion curve $\omega = \omega(k)$ of the polariton can cross at a certain k the dispersion curve of the biphonon. In this case, a polariton Fermi resonance takes place. According to the theory of Agranovich and Lalov,[2] resonant interaction of a polariton with a biphonon leads to a substantial change of the shape of the polariton dispersion curve, and also to the appearance of an energy gap near the biphonon frequency. So far, convincing data on the existence of biphonons were obtained only for a small number of crystals (see, e.g., Ref. 3).

Particular interest attaches to investigations of bound states in diatomic cubic crystals. Evaporation spectrum of the lattice contains in this case a single threefold degenerate fundamental vibration [which splits into a doublet of a longitudinal (LO) and transverse (TO) vibrations]. thereby greatly simplifying the identification of the biphonon line in the Raman-scattering (RS) spectra One such crystal is gallium phosphide. Earlier investigations of RS in GaP (see, e.g., Refs. 4 and 5) have shown that the TO-vibration line of the RS of GaP has an anomaly: it is asymmetrical and greatly broadened compared with the LO line. This fact was discussed in Refs. 5–7, but the question of the causes of the anomaly remained open.

Investigations of the polarization-angular distribution of the RS in a GaP crystal, carried out by us earlier,[8] have shown that the cause of the anomaly is the biphonon RS line located in the region of the wing of the TO line. In this paper we report further investigations of the biphonon in this crystal under conditions of polariton Fermi resonance. The experimental results are compared with the theory[9] of the density of RS by a biphonon in the presence of Fermi resonance between a biphonon and a polariton.

2. FREQUENCY-ANGULAR DEPENDENCE AND ANGULAR DISTRIBUTION OF THE RS INTENSITY

The theory[1,2,9] makes it possible to calculate the angular dependences of the frequency and of the intensity of the polariton under conditions of Fermi resonance with a biphonon. In the case of the GaP crystal, whose lattice has one dipole-active fundamental vibration and one dipole-active bound state, the angular dependence of the polariton frequency is of the form[7]

$$k_p^2 = \frac{\omega_p^2}{c^2}\left(\varepsilon_\infty + \frac{S\omega_{TO}^2}{\omega_{TO}^2-\omega_p^2} + \frac{S'(\omega')^2}{(\omega')^2-\omega_p^2}\right), \tag{1}$$

where k_p and ω_p are respectively the polariton wave vector and frequency; ω_{TO} and ω' are the frequency of the TO components of the fundamental vibration and of the biphonon, respectively; c is the velocity of light in vacuum; S is the oscillator strength of the fundamental vibration; ε_∞ is the high-frequency dielectric constant of the crystal, and S' is the oscillator strength of the biphonon. The values of the wave vector k_p of the polariton is determined by the momentum conservation law

$$k_p^2 = k_0^2 + k_s^2 - 2k_0k_s\cos\theta, \tag{2}$$

where k_0 and k_s are the wave vectors of the corresponding incident and Stokes scattered radiation, and θ is the angle between $\mathbf{k}_0$ and $\mathbf{k}_s$.

An experimental investigation of the relation (1) yields convincing proof of the existence of the biphonon. In addition, this investigation makes it possible to de-

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termine the oscillator strength of the biphonon, its LO and TO splitting, and other parameters.

The angular dependence of the intensity of the RS under conditions of polariton Fermi resonance was investigated theoretically in Ref. 9. It was found that the ratio of the intensities of the RS and of the exciting radiation, called the effective RS cross section (per unit length of the crystal and in a unit scattering solid angle) depends on the angle between $\mathbf{k}_0$ and $\mathbf{k}_s$ in the following manner:

$$\sigma(\theta)=\omega_p a_1^2 \Big/ \left[n_p^2+\frac{\omega_p}{2}\frac{\partial n_p^2}{\partial \omega_p}-\frac{c}{u_s\omega_p}(\omega_0 n_0\cos\theta-\omega_s n_s)\right], \qquad (3)$$

where $\sigma(\theta)$ is the effective RS cross section per unit length of the crystal and in a unit solid scattering angle:

$$a_1=\bar{\chi}\frac{\omega_s^2}{c^2}\left(\frac{2\pi\hbar n_s}{n_0}\right)^{1/2}+\sum_{f=1,2}\frac{N_f\omega_f^2}{\omega_f^2-\omega_p^2},$$

$$N_f=\left(\frac{S_f\sigma_f}{\omega_f}\right)^{1/2}\operatorname{sign}\beta_f,$$

$$\beta_f=\sum_{\nu}\alpha^{(f\nu)}(\mathbf{e}_p,\mathbf{e}_\nu), \quad \alpha^{(f\nu)}=e_s^i\alpha_{ij}^{(f\nu)}e_0^j.$$

The subscripts 0, s, and p refer respectively to the exciting, Stokes, and polariton waves, $\bar{\chi}$ is the contribution of the energy levels that are far from ω_f to the nonlinear susceptibility χ:

$$\chi=e_s^i e_p^j e_0^k\chi_{ijk},$$

χ_{ijk} is the tensor of the nonlinear susceptibility, $n_{0,s}$ is the refractive index at the corresponding wavelength, the index f numbers the dipole-active vibrations, S_f is the oscillator strength, σ_f is the effective RS cross section far from the polariton region, $\alpha_{ij}^{(f\nu)}$ is the RS tensor per cell, $\mathbf{e}$ are the polarization unit vectors,

$$n_p^2=\varepsilon_\infty+\sum_{f=1,2}\frac{S_f\omega_f^2}{\omega_f^2-\omega_p^2}, \quad u_s=|\nabla_{k_s}\omega_s|.$$

The index ν numbers the mutually degenerate vibrations with frequency ω_f.

The relation (3) was not verified experimentally. We report here the first such investigation, with GaP as the example.

3. EXPERIMENTAL TECHNIQUE, RESULTS, AND DISCUSSION

The RS spectra of the GaP crystal were excited by radiation of wavelength $\lambda=578.2$ nm from a copper-vapor laser. The spectra was registered with a DFS-12 spectrometer at a sample temperature $T=80$ K. The investigated GaP sample was a right prism with dimensions ~1 cm and with faces oriented in the directions [100], [010], and [001]. The exciting radiation propagated in the crystal at small angles θ to the [100] direction. The angle θ was varied by changing the direction of $\mathbf{k}_0$, with $\mathbf{k}_s$ fixed. The value of θ was determined accurate to the sum of the apertures $\Delta\theta=0.5°$ of the beams of the incident and scattered radiation. In the indicated experimental geometry, the TO excita-

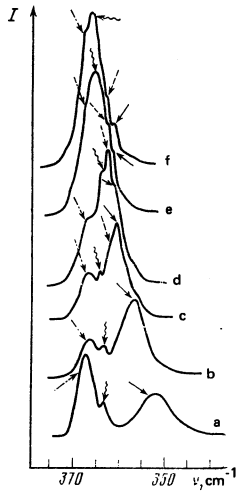

FIG. 1. RS spectra of GaP crystal at different angles θ between the wave vectors $\mathbf{k}_0$ and $\mathbf{k}_2$: a) θ +1.8°, k_p = 2070 cm^{-1}; b) θ = 2.5°, k_p = 2840 cm^{-1}; c) θ = 3.0°, k_p = 3140 cm^{-1}; d) θ = 3.4°, k_p = 3500 cm^{-1}; e) θ = 4.5°, k_p = 4460 cm^{-1}; f) θ = 5.5°, k_p = 5400 cm^{-1}. Sample temperature T = 80 K. Spectral width of the slit 1.0 cm^{-1}. A straight arrow denotes a low-frequency polariton, a wavy arrow a high frequency polariton, a dashed arrow the LO component of the biphonon, and a dash-dot arrow pertains to the fundamental TO vibration. The intensities of the spectra a, b and c are magnified 4.2 and 1.2 times, respectively, compared with the actual intensity.

dash-dot arrow, as well as two peaks with frequencies $\omega=363$ cm^{-1} (wavy arrow) and $\omega=352$ cm^{-1} (straight arrow). With increasing angle between k_0 and k_s (i.e., with increasing k_p), a frequency shift is observed as well as a change of the intensities of the indicated peaks (Figs. 1b–1f). This makes it possible to identify the observed intensity peaks with polariton excitations. In addition, with increasing k_p, as indicated earlier,[8] the Fermi-resonance conditions are improved, and this increases the intensity of the LO component of the biphonon (dashed arrow, $\omega=353$ cm^{-1}).

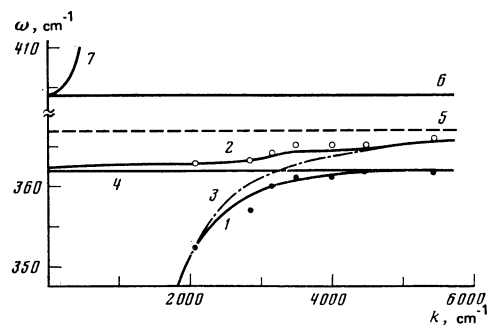

FIG. 2. Dispersion curves of the excitations of a crystal lattice under conditions of Fermi resonance of fundamental polariton with a biphonon. The solid curves were calculated from Eq. (1). The numbers denote the dispersion curve: 1) of the low-frequency polariton, 2) of the high-frequency polariton, 3) of the fundamental polariton in the absence of Fermi resonance with the biphonon, 4) of the biphonon in the absence of Fermi resonance with the fundamental polariton, 5 and 6) of the fundamental TO (far from the polariton region) and LO phonons, 7) of the photon polariton. The light and dark circles are respectively the experimental results for high-frequency and low-frequency polaritons.

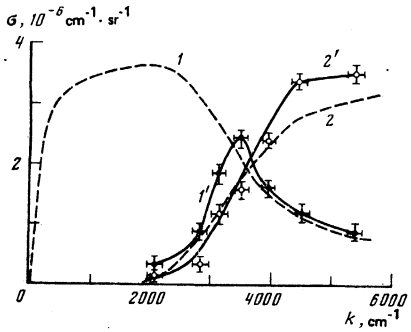

FIG. 3. Dependence of the effective cross section of the Raman scattering on the wave vector of the polariton: 1) and 2) curves calculated from Eq. (3) for the low-frequency and high-frequency and high-frequency polaritons, respectively. Curves 1′ and 2′ were plotted using the experimental points denoting the relative intensities referred to identical conditions for the low-frequency and high-frequency polaritons, respectively.

tions of the lattice were significantly suppressed. This made it possible to obtain a satisfactory resolution of the biphonon line, whose frequency differed by only 5 cm^{-1} from the frequency of the fundamental TO phonon.

The obtained RS spectra are shown in Figs. 1a–1f. The spectrum 1a corresponds to the smallest of the measured values of k_p. A weakened line of fundamental TO vibration is observed here, designated by a

The frequencies ω_p of the polaritons and the corresponding values of the wave vectors k_p, obtained in experiment, are shown in Fig. 2. The values of ω_p and k_p, which pertain to the polariton with the lower frequency, made up the dispersion branch 1, while ω_p and k_p of the higher-frequency polariton made up the dispersion branch 2. (These polaritons are referred to hereafter as "low-frequency" and "high-frequency.") The solid lines show the theoretical dispersion relation (1). To obtain the best agreement between the theoretical curve and the experimental points, the oscillator strengths S and S' were varied subject to the conditions $S+S'=1.93$. Such an agreement was obtained at $S=1.68$ and $S'=0.25$. The dispersion relation (1) with the biphonon disregarded ($S=1.93$, $S'=0$) is shown in Fig. 2 by dash-dot curve 3. As follows from Fig. 2, the presence of Fermi resonance between the fundamental polariton and the biphonon at $k_p=3200$ cm^{-1} changed substantially the dispersion relation and led to formation of an energy gap in the region of the biphonon frequency.

The results of the investigation of the angular dependence of the RS intensity are shown in Fig. 3. The dashed curves 1 and 2 constitute the theoretical angular dependence (3) of the effective cross section of RS of polaritons. The solid curves 1′ and 2′ are the results of the experiment. Curves 1, 1′ and 2, 2′ correspond respectively to the low-frequency and high-frequency polaritons. The experimental points are designated in the former case by dark circles and in the latter by light circles.

When plotting the theoretical curves 1 and 2 we used the following data: $\omega_{TO}=367$ cm^{-1}, $\omega_{LO}=404$ cm^{-1}, $\omega'=362$ cm^{-1} (biphonon frequency), intensity ratio $I_{LO}/I_{biph}=8.5$,[8] effective cross section far from the polariton region $\sigma_{TO}=3.5\times10^{-6}$ $cm^{-1}\cdot sr^{-1}$; $\varepsilon_\infty=9.09$, $n_0\approx n_s=3.25$, $\mathrm{sign}\,\beta_f=1$.[9]

The experimental points of curves 1′ and 2′ on Fig. 3 are the values of the intensity of the RS of the polaritons relative to the intensty of the "standard" fundamental LO vibration line. (It is known that the frequency and intensity of the LO vibrations remain unchanged with changing scattering angle.) The normalization of the relative intensities was chosen in the following manner. It was assumed that at $k_p=6000$ cm^{-1} the polariton effect is negligible. Consequently, the value of the intensity of the high-frequency polariton is close to the value of the intensity of the fundamental TO phonon far from the polariton region (see also Fig. 2, curve 2). On the whole, the agreement of the theory with experiments is satisfactory. However, as follows from Fig. 3, the theory[9] calls apparently for a more detailed allowance for the mechanism of light scattering by bound states.

Thus, polariton Fermi resonance makes it possible to investigate not only qualitative but also quantitative parameters of bound states. This effect makes it also possible to verify experimentally the theoretical notions concerning the processes of light scattering by nonfundamental excitations of the crystal lattice.

[1]J. Ruvalds and A. Zawadowski, Phys. Rev. **B2**, 1171 (1970).
[2]V. M. Agranovich and I. I. Lalov, Fiz. Tverd. Tela (Leningrad) **13**, 632 (1971) [Sov. Phys. Sol. State **13**, 859 (1971)].
[3]V. S. Gorelik, G. G. Mitin, and M. M. Sushchinskiĭ, Zh. Eksp. Teor. Fiz. **69**, 843 (1975) [Sov. Phys. JETP **42**, 419 (1975)]. G. G. Mitin, V. S. Gorelik, and M. M. Sushchinskiĭ, Fiz. Tverd. Tela (Leningrad) **16**, 2956 (1974) [Sov. Phys. Solid State **16**, 1972 (1975)].
[4]V. S. Gorelik, O. G. Zolutukhin, and M. M. Sushchinskiĭ, Zh. Prikl. Spektrosk. **28**, 495 (1978).
[5]B. Kh. Bairamov, O. E. Kitaev, V. K. Negodulko, and Z. M. Khashkoshev, Fiz. Tverd. Tela (Leningrad) **16**, 1129 (1974) [Sov. Phys. Sol. State **16**, 725 (1974)].
[6]I. B. Levinson and I. L. Maksimov, Pis'ma Zh. Eksp. Teor. Fiz. **23**, 3 (1976) [JETP Lett. **23**, 1 (1976)].
[7]B. N. Mavrin, and Kh. E. Sterin, in: Sovremennye problemy spektroskopii kombinatsiannogo rasseyaniya sveta (Contemporary Problems in the Spectroscopy of Raman Scattering of Light), Nauka, 1978, p. 48.
[8]V. S. Gorelik, O. G. Zolotukhin, and M. N. Sushchinskiĭ, Kratk. soobshch. po fiz. No. 2, 3 (1980).
[9]V. L. Strizhevskii, Zh. E. Ponat, and Yu. N. Yashkir, Opt. Spektrosk. **31**, 388 (1971).

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