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Dispersion of Phonon Surface Polaritons in ZnGeP₂: Anisotropy and Temperature Impacts

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Abstract

Zinc germanium diphosphide (ZnGeP₂) is an attractive and promising functional material for different devices of the nano- and optoelectronics. In this paper, dispersion of phonon surface polaritons (PSPs) in ZnGeP₂ has been studied in the 200–500-cm⁻¹ spectral range at 4 and 300 K. Dispersion of “real” and “virtual” PSPs were calculated for C-axis being normal and parallel to the surface. Anisotropy in ZnGeP₂ leads to the different numbers of PSP dispersion branches for different orientations of the sample. The temperature-dependent phonon contributions in the dielectric permittivity shift dispersion of the surface polaritons in ZnGeP₂ to the higher wavenumbers at 4 K. We have shown that experimental dispersion of PSP is in agreement with theory.

Keywords: Single crystal, Phonon, Surface polariton, Anisotropy, Low temperature

Background

In this study, we report on the impact of anisotropy and low temperature on the dispersion of surface polaritons in zinc germanium diphosphide (ZnGeP₂), which is a promising material for the nano- and optoelectronics.

Introduction

Among other ternary A^{IV}B^{IV}C₂^V compounds, ZnGeP₂ stands out for its properties, such as great values of the coefficients of the nonlinear susceptibility and birefringence, which attract interest of researches.

Mechanical stability, resistance to moisture, aggressive environments, and good thermal conductivity characterize ZnGeP₂ as an attractive and promising functional material for different devices of the nano- and optoelectronics. In [1], it has been discussed that diphosphides can be used in infrared converter systems. Experimental results of [2] prove that replacing CdTe by diphosphides can increase efficiency of the solar converters and simplify their mass deployment.

Therefore, the study of optical properties of ZnGeP₂ is crucial for industrial applications of this material.

In the previous paper [3], we have reported on the lattice vibration behaviors of ZnGeP₂ single crystals derived from the far-infrared (FIR) reflectance spectra in the temperature range of 4–300 K. From [3], one can notice that optical phonon behaviors in ZnGeP₂ at low temperatures are similar to those in other diphosphides [4, 5]. These results show that surface polaritons in ZnGeP₂ can be excited in the number of spectral ranges. However, for ZnGeP₂, the surface polaritons practically have not been studied yet. Results of [6] have shown that temperature has an impact on the dispersion of surface phonon polaritons in binary diphosphide Zn₃P₂.

Here, we present the results of our study of the dispersion of the surface polaritons in ZnGeP₂ at different temperatures.

Methods

In the experiments, a set of samples of single crystals of ZnGeP₂ cut into plates of size 2 × 4 × 0.5 mm was used. The samples of ZnGeP₂ were oriented to (001) and (100) crystallographic planes. The orientation of the crystallographic planes was controlled by X-ray diffraction.

As an input data for the calculations of the dispersion of phonon surface polariton (PSP), we used reflectance

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data of ZnGeP₂ from our study [3]. These spectra were measured at 300 K in the 200–500-cm⁻¹ range, using a Bruker IFS 66v/s spectrometer with Hg lamp as the source of radiation with a resolution of 0.5 cm⁻¹, 256 scans per 20 s employing polarized radiation were collected in each experiment. The temperature of sample varied in the 4–300-K temperature range. The angle of incidence of radiation was less than 10°. Spectra were measured at two orientations of the electrical vector *E* of the IR radiation with respect to the crystal: *E*||*c* and *E*⊥*c*.

The method of attenuated total reflection (ATR) was firstly used for the excitation of surface waves in metals [7]. Since general principles of excitation of PSP by ATR have been described in [8], this method remains the easiest and the most reliable for excitation of surface polaritons.

We obtained the ATR spectra of PSP for ZnGeP₂ in the 300–500-cm⁻¹ frequency range using polarized radiation. To measure these data, we used FTIR spectrometer Bruker IFS 66 with accessory with grazing angle of the incidence equipped by Ge hemisphere as ATR element. The air gap between the investigated sample and the hemisphere varied from 1.5 to 2 μ.

Results and Discussion

In the tetragonal ZnGeP₂, B₂ (can be observed employing the radiation polarized parallel to the *c*-axis) and E (the radiation polarized normal to the *c*-axis) modes are

infrared active. According to the data from [3], in the 200–500-cm⁻¹ range, one can observe two B₂ and four E modes. Spectral analysis of the reflectance data has been performed employing factorized model for the dielectric permittivity in the following form:

$$\epsilon(\nu) = \epsilon_\infty \prod_{j=1}^n \left(\frac{\nu^2 + i\gamma_{jl}\nu - \nu_{jl}^2}{\nu^2 + i\gamma_{jt}\nu - \nu_{jt}^2} \right), \tag{1}$$

where ε_∞ is high-frequency dielectric permittivity and ν_{jl} and γ_{jl} (ν_{jt} and γ_{jt}) are the frequency and damping coefficient of the *j*th longitudinal (transversal) mode. Dispersion of the real part of the dielectric permittivity of ZnGeP₂ obtained using model (1) at 4 and 300 K is presented in Fig. 1.

Results of spectral analysis of the reflectance data of ZnGeP₂ at 4 and 300 K are shown in Table 1. Observed temperature shift of the phonon modes is in agreement with theoretical calculations from [9] and has been also observed in the reflectance spectra of Al₂O₃ [10] and Raman spectra of Si, Ge, and α-Sn [11].

Before discussing the obtained results, we make a short review of influence of the anisotropy on the dispersion relation of PSP. The coordinate axes *x* and *y* lay in the sample’s plane, and *z* is normal to the surface. Let us denote the component of the dielectric tensor which is normal (parallel) to the optical axis of

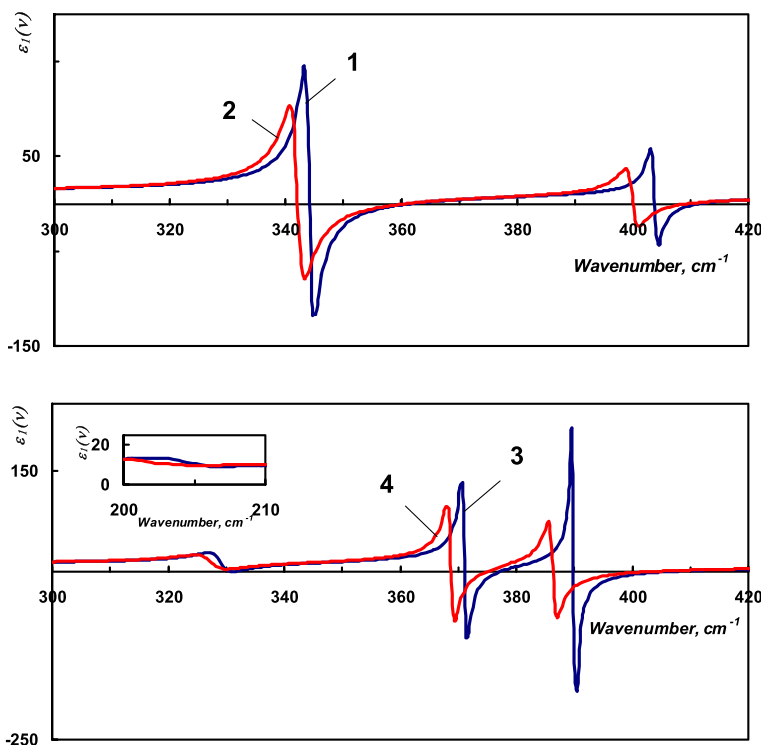


Fig. 1 Real part of the dielectric function of ZnGeP₂ single crystal. *E*||*c*: 1 4 K, 2 300 K; *E*⊥*c*: 3 4 K, 4 300 K

Table 1 Input data for ZnGeP₂

<i>B</i> ₂ modes										
4 K				300 K						
	ϵ_∞	ν_L, cm^{-1}	γ_L, cm^{-1}	ν_T, cm^{-1}	γ_T, cm^{-1}	ϵ_∞	ν_L, cm^{-1}	γ_L, cm^{-1}	ν_T, cm^{-1}	γ_T, cm^{-1}
	10.68					10.04				
1		362	2.0	343	1.9		361	2.1	340	3.5
2		412	2.2	403	1.1		409	2.8	400	1.8
<i>E</i> modes										
4 K				300 K						
	ϵ_∞	ν_L, cm^{-1}	γ_L, cm^{-1}	ν_T, cm^{-1}	γ_T, cm^{-1}	ϵ_∞	ν_L, cm^{-1}	γ_L, cm^{-1}	ν_T, cm^{-1}	γ_T, cm^{-1}
	10.05					10.04				
1		205	12.0	205	16.0		203	5.7	203	6.8
2		334	5.8	329	3.6		332	4.8	328	6.2
3		378	2.4	371	0.9		375	2.1	368	0.7
4		403	1.5	388	1.1		399	2.7	385	1.3

the crystal as ϵ_\perp (ϵ_\parallel). Neglecting the damping, we have analyzed this dielectric function applying conditions described in [8] and found spectral ranges of existence of the “real” (type 1) and “virtual” (type 2) PSP in ZnGeP₂ at 4 and 300 K, which are shown in Table 2.

In the case of uniaxial media, according to the terminology of [6], “ordinary” PSP occurs when the optical axis *C* is parallel to the surface (*C*||*y*). The dispersion relation in this case ($\epsilon_x = \epsilon_z = \epsilon_\perp$) is as follows:

$$K^2 = \epsilon_\perp(\nu) / (\epsilon_\perp(\nu) + 1). \tag{2}$$

This dispersion relation involves only ϵ_\perp , and it is of the same form as for PSP dispersion in isotropic media.

“Extraordinary” PSP occur in the two other configurations. The optical axis is perpendicular to the surface (*C*||*z*). The dispersion relation can be written down as follows:

$$K^2 = (\epsilon_\parallel(\nu)(1 - \epsilon_\perp(\nu))) / ((1 - \epsilon_\perp(\nu))\epsilon_\parallel(\nu)), \tag{3}$$

where $\epsilon_z = \epsilon_\parallel$, $\epsilon_x = \epsilon_\perp$. The optical axis is parallel to the surface of the sample and is parallel to the direction of propagating of PSP (*C*||*x*)

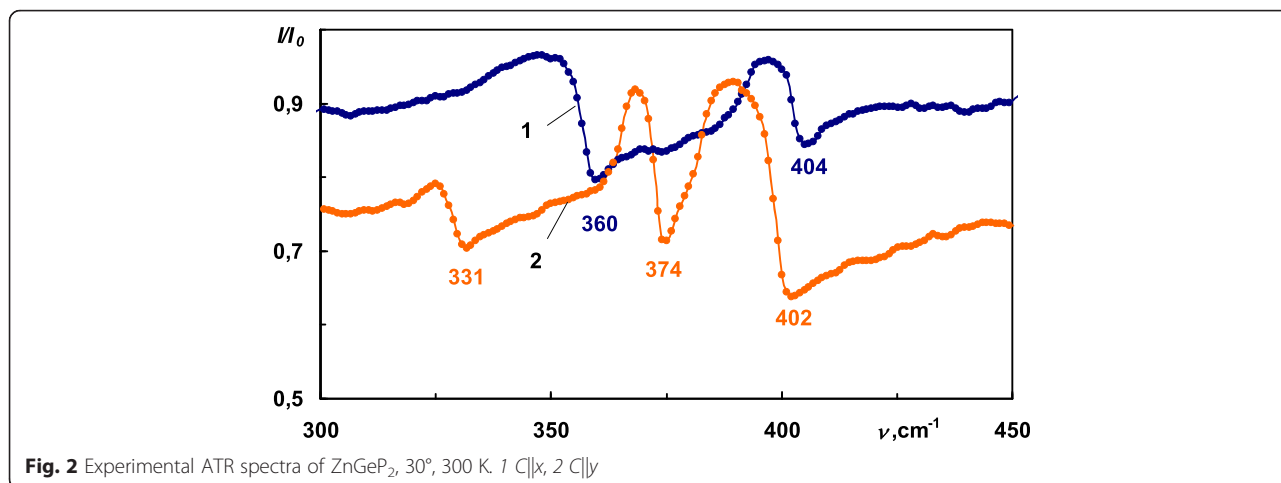
$$K^2 = (\epsilon_\perp(\nu)(1 - \epsilon_\parallel(\nu))) / ((1 - \epsilon_\perp(\nu))\epsilon_\parallel(\nu)), \tag{4}$$

with $\epsilon_x = \epsilon_\parallel$, $\epsilon_z = \epsilon_\perp$.

Experimental evaluation of the dispersion of surface polaritons has been performed applying the method of ATR, which was used for excitation of the surface waves in ZnGeP₂ for *C*||*x* and *C*||*y* orientation of the sample at several angles of the incidence. Figure 2 presents experimental ATR spectra recorded at 30°. In the presence of the SP damping and dissipation of the electromagnetic wave energy, spectra show certain number of minima, whose wavenumbers correspond to the PSP. In Fig. 3, we show three experimental and five calculated ATR spectra (*C*||*y*) as the so-called ATR surface $R(\nu, \alpha)$, which is a three-dimensional presentation of the system transmission that depends on the radiation frequency ν and angle α . This ATR surface $R(\nu, \alpha) = I(\nu, \alpha) / I_0(\nu, \alpha)$ has three “canyons” connected with a “pass.” $I(\nu, \alpha)$ is the intensity of radiation passing through the “ATR

Table 2 Ranges of existence of PSP in ZnGeP₂

	<i>C</i> <i>x</i>	<i>C</i> <i>y</i>	<i>C</i> <i>z</i>
SPP 1		4 K	
	$\nu = 404 \div 406 \text{ cm}^{-1}$	$\nu = 329 \div 332 \text{ cm}^{-1}$ $\nu = 369 \div 374 \text{ cm}^{-1}$ $\nu = 386 \div 401 \text{ cm}^{-1}$	$\nu = 400 \div 403 \text{ cm}^{-1}$
		300 K	
	$\nu = 400 \div 403 \text{ cm}^{-1}$	$\nu = 327 \div 331 \text{ cm}^{-1}$ $\nu = 371 \div 376 \text{ cm}^{-1}$ $\nu = 390 \div 404 \text{ cm}^{-1}$	$\nu = 404 \div 406 \text{ cm}^{-1}$
SPP 2		4 K	
	$\nu = 344 \div 363 \text{ cm}^{-1}$ $\nu = 406 \div 409 \text{ cm}^{-1}$		$\nu = 201 \div 203 \text{ cm}^{-1}$ $\nu = 327 \div 331 \text{ cm}^{-1}$ $\nu = 369 \div 374 \text{ cm}^{-1}$ $\nu = 386 \div 399 \text{ cm}^{-1}$
		300 K	
	$\nu = 342 \div 360 \text{ cm}^{-1}$ $\nu = 408 \div 412 \text{ cm}^{-1}$		$\nu = 204 \div 205 \text{ cm}^{-1}$ $\nu = 329 \div 333 \text{ cm}^{-1}$ $\nu = 371 \div 377 \text{ cm}^{-1}$ $\nu = 390 \div 403 \text{ cm}^{-1}$



element-gap-sample” system; $I_0(\nu, \alpha)$ is the intensity of the incident radiation onto the ATR unit. The depth of the “canyon” depends on the following system parameters: gap d between the ATR element and sample, radiation frequency ν , complex permittivity $\epsilon(\nu, k)$ of the sample, and the refractive indexes of the ATR unit and gap. The surface polariton dispersion curves $\nu_s(k)$ correspond to the “canyons”, i.e., to the set of ATR spectra minima. (Here, ν_s is the surface polariton frequency and k is the SP wave vector). Thus, we can distinguish three branches of PSP dispersion in ZnGeP_2 within the measured spectral range. From the minima of ATR spectra, the PSP dispersion has been evaluated:

$$k = (2\pi\nu/c) n \sin\alpha, \tag{5}$$

where ν is the frequency of the ATR spectrum minimum, c is the speed of light in a vacuum, and n is the refractive index of material of the ATR element.

We have calculated dispersion of PSP in ZnGeP_2 for three possible configurations applying Eqs. 2–4 in the spectral ranges shown in Table 2 at 4 and 300 K. We present the obtained PSP dispersion branches in Figs. 4, 5, and 6. To emphasize the influence of the temperature, we plot 4 K PSP dispersion curves in blue and 300 K in orange.

For configuration $C||x$, we obtained one branch of the dispersion of the “real” PSP and two branches of the dispersion of the “virtual” PSP. The “real” PSP branch goes to the infinity wave vector within the specified spectral range. The “virtual” dispersion branches terminate at the cross points of the polariton dispersion with the dispersions of the longitudinal optical phonons:

1. 412 cm^{-1} , 4 K; 409 cm^{-1} , 300 K;
2. 362 cm^{-1} , 4 K; 361 cm^{-1} , 300 K.

As already mentioned, for $C||y$, the dispersion relation is similar to the isotropic case, since only ϵ_{\perp} is involved

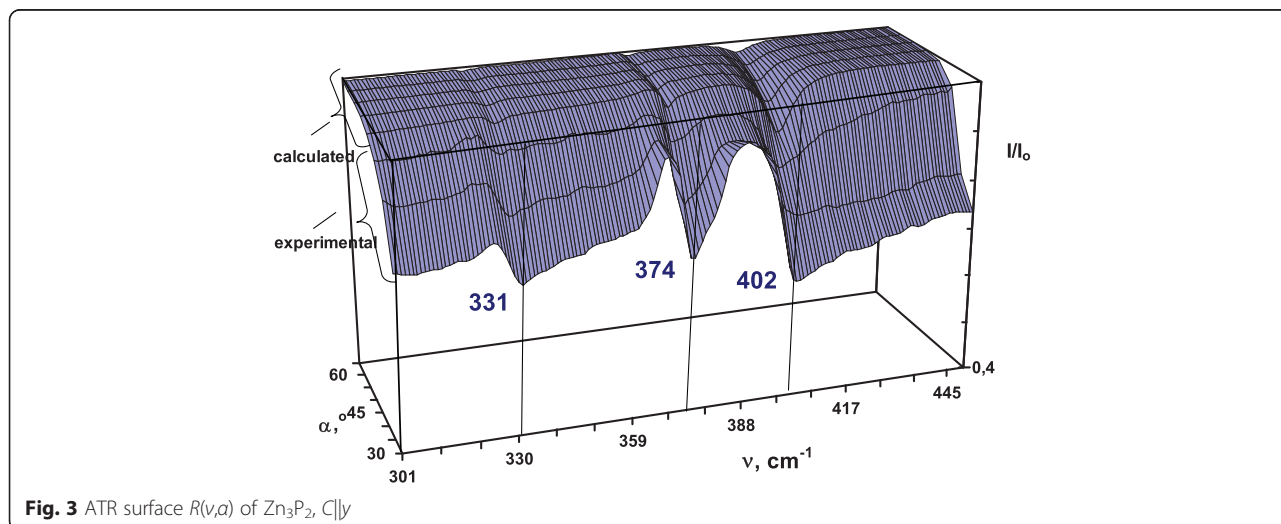


Fig. 3 ATR surface $R(\nu, \alpha)$ of Zn_3P_2 , $C||y$

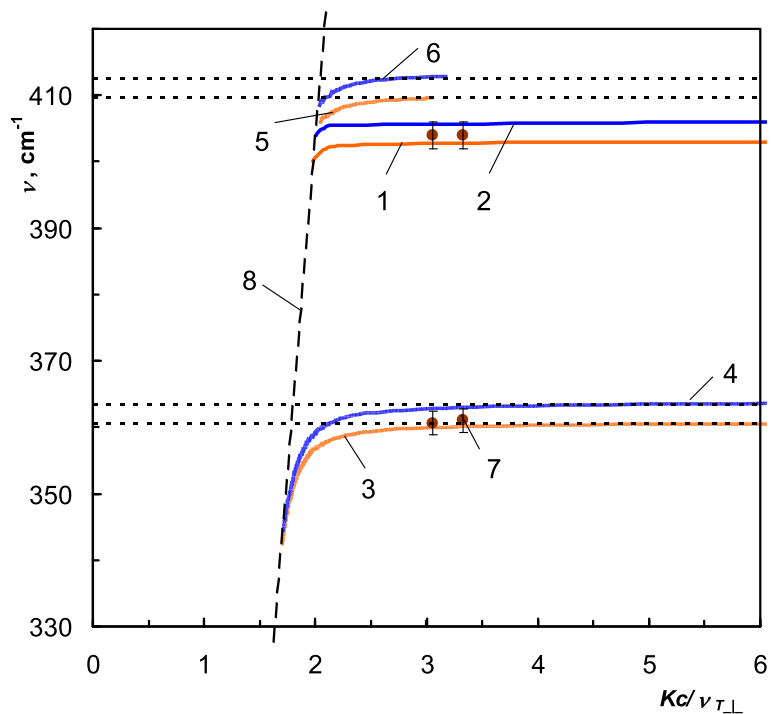


Fig. 4 Dispersion of the PSP in $\text{ZnGeP}_2, \text{C}||x$. "Real" PSP: 1 300 K, 2 4 K; "virtual" PSP: 3, 5 300 K, 4, 6 4 K; 7 experimental "real" PSP, 300 K, 8 "light line"

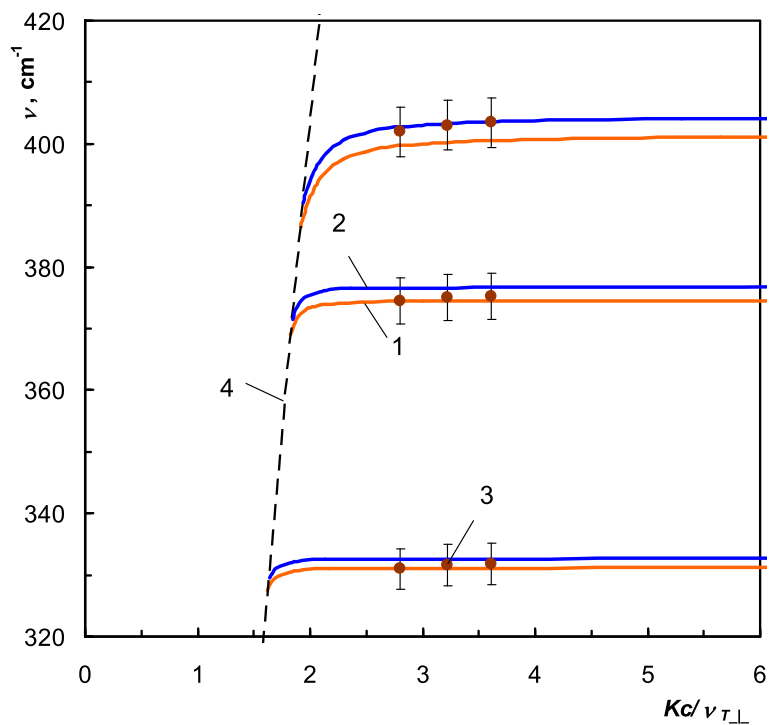
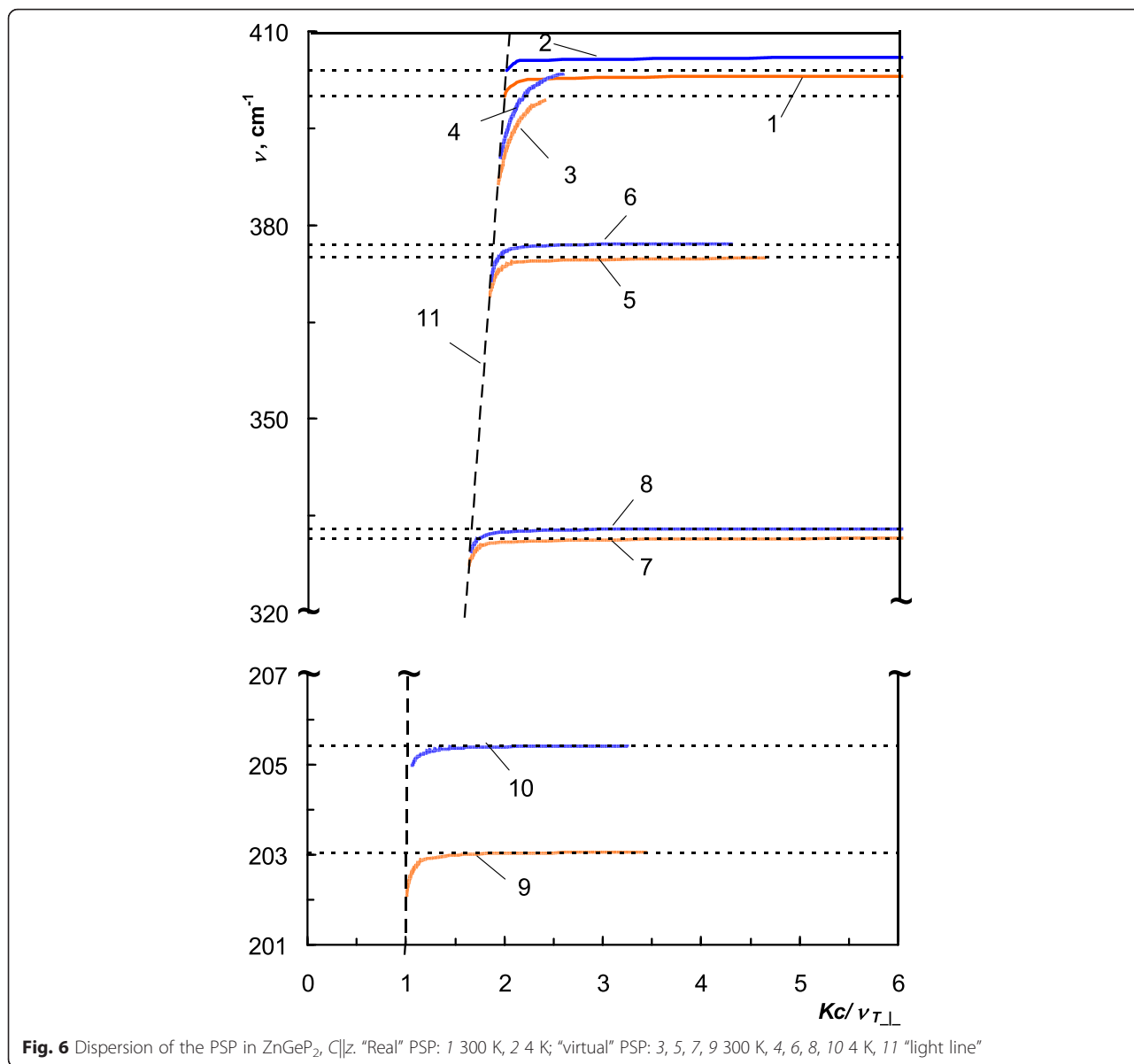


Fig. 5 Dispersion of the PSP in $\text{ZnGeP}_2, \text{C}||y$. 1 "real" PSP, 300 K; 2 "real" PSP, 4 K; 3 experimental "real" PSP, 300 K; 4 "light line"



in Eq. (2). Therefore, the quantity of dispersion branches is equal to the quantity of the Reststrahlen bands for $E \parallel c$. We obtained three dispersion branches of "real" PSP for $C||y$ orientation.

We have obtained five PSP dispersion branches for $C||z$ case: one branch of the dispersion of the "real" PSP and four branches of the dispersion of the "virtual" PSP, which terminate at the cross points of the polariton dispersion with the dispersions of the longitudinal optical phonons:

1. 203 cm⁻¹, 4 K; 205 cm⁻¹, 300 K;
2. 332 cm⁻¹, 4 K; 334 cm⁻¹, 300 K;
3. 375 cm⁻¹, 4 K; 378 cm⁻¹, 300 K;

4. 399 cm⁻¹, 4 K; 403 cm⁻¹, 300 K.

Due to the temperature shift of the phonon frequencies of ZnGeP₂ to the higher wave numbers [3], almost all branches of the 4 K dispersion lay above the corresponding branches at 300 K. The temperature-dependent phonon contributions in the dielectric permittivity, which are described by frequency, damping, and strength in frames of Lorentz model [3], affect dispersion of the surface polaritons in ZnGeP₂.

As one can notice in Figs. 4, 5, and 6, experimental PSP dispersion at 300 K calculated using Eq. (5) and shown in dots is a good agreement with the corresponding calculated dispersion branches. This

agreement serves as a confirmation of 4 K PSP dispersion branches in ZnGeP_2 which were calculated in the same manner.

Conclusions

Thus, in this paper, dispersion of PSP in ZnGeP_2 has been studied in the $200\text{--}500\text{-cm}^{-1}$ spectral range at 4 and 300 K. Dispersion of “real” and “virtual” PSP were calculated for *C*-axis being normal and parallel to the surface. Anisotropy in ZnGeP_2 leads to the different numbers of PSP dispersion branches for different orientations of the sample. The temperature-dependent phonon contributions in the dielectric permittivity shift dispersion of the surface polaritons in ZnGeP_2 to the higher wave numbers at 4 K. Experimental dispersion of PSP is in agreement with theory.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

KS performed the measurements and drafted the manuscript. KS, AO, and EV discussed the results. AO helped to draft the manuscript. All authors read and approved the final manuscript.

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