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# Spectroscopy of the Surface Polaritons in the $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$ Solid Solutions

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## Abstract

Here we report on the analysis of the effect of the doping of  $\text{CdP}_2$  single crystals by  $\text{ZnP}_2$  nanoclusters on the dispersion of the surface polaritons (SP). The ATR spectroscopic technique has been applied to excite the SP in the  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  system. Analysis of the obtained spectra has shown that the doping of  $\text{CdP}_2$  single crystals by  $\text{ZnP}_2$  nanoclusters result in the position and the width of the dispersion branches of the SP. This effect is more pronounced in the low frequency dispersion branches. These SP branches are originated from phonons which correspond to the motion of the cation sublattice.

**Keywords:** Nanocluster, Solid solution, Vibrational properties, Surface polaritons, ATR

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## Background

The recent interest to exploring the properties of zinc and cadmium diphosphides  $\text{ZnP}_2$  and  $\text{CdP}_2$  is caused by the possibility of employing them in various devices, such as, temperature detectors, deflectometers of laser beams, photoconducting cells, magnetic sensors, extenders, and stabilizers of laser radiation, photovoltaic applications [1, 2]. Vibrational properties of  $\text{ZnP}_2$  and  $\text{CdP}_2$  have been previously reported in [3–6] in the wide temperature range. The effect of the doping of  $\text{CdP}_2$  by  $\text{ZnP}_2$  nanoclusters on the vibrational properties of the resulting solid solutions of  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  have recently been presented in [7]. According to the technology of the obtaining  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  solid solutions, most of the  $\text{ZnP}_2$  nanoclusters are located in the near surface area. It has been shown [8], that surface polaritons are very sensitive to the presence of the surface defects and impurities. The dispersion and the damping of surface polaritons, that are localized in a thin surface layer with the thickness of the order of the reciprocal value of the damping constant, are very sensitive to the characteristics of the surface including the structure of the crystal and its relief [9]. It was shown that the optical spectroscopy is a powerful

experimental technique to study the properties of complex structures [10, 11], and the most efficient way to obtain the data on the dispersion of SP in solid solutions is employing ATR technique, as it has been shown in [9] for  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  and  $\text{GaAs}_x\text{P}_{1-x}$ . Thus, present work is aimed to study the influence of  $\text{ZnP}_2$  nanoclusters on the dispersion of the SP in  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  solid solutions. This might provide information on the distribution of the  $\text{ZnP}_2$  nanoclusters in the host  $\text{CdP}_2$  that can be useful for employing  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  in the construction of the optoelectronic devices.

The paper consists of the following parts: Introduction briefly represents the previous results and describes the motivation of the research. Experimental section procedures work, we describe the experimental procedures, such as preparing the samples, optical spectra measurements, and their treatment. In the Results and Discussion section we describe the influence of the doping  $\text{CdP}_2$  by the  $\text{ZnP}_2$  nanoclusters on the dispersion of SP in  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  by the analysis of the systematic changes in the ATR spectra. In Conclusions section we summarize obtained results.

## Methods

$\text{CdP}_2$  in the polycrystalline form was grown from the initial elements by two-temperature way and then was used to grow single crystals of  $\text{CdP}_2$ . The  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  solid

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solution was obtained in the following way: Zn was deposited on the surface of the  $\text{CdP}_2$  single crystal and then annealed in the oven at the temperature of  $650^\circ\text{C}$  for 600 h. The  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  system is a  $\text{CdP}_2$  single crystal with inclusions of tetragonal  $\text{ZnP}_2$  with size of up to 100 nm [1]. The concentration of  $\text{ZnP}_2$  nanoclusters has been controlled by XRF, and in the studied  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  sample it was  $x = 0.9991$ . As a reference, in this work we also used pure  $\text{CdP}_2$  ( $x = 1$ ) samples. All studied samples were in the shape of plates with a size of  $2 \times 3 \times 1$  mm.

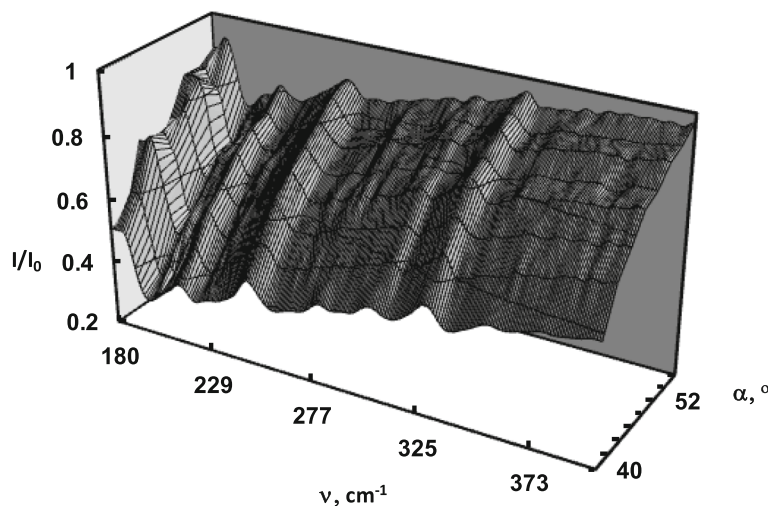
The ATR spectra of the SP were recorded in the usual manner in the  $150 - 500 \text{ cm}^{-1}$  frequency range. In the experiments, we used p-polarized radiation and spectrometers KSDI-82 equipped with ATR unit LOMO NPVO-1 as well as Bruker IFS 88 equipped with Perkin Elmer ATR unit. CsI semicylinder served as ATR element in both cases. ATR spectra were recorded with several angles of the incidence of the radiation in the range of  $40 - 60^\circ$ . The polystyrene spacers were used to make an air gap between the investigated sample and the semicylinder, it was varied from 6 to 8  $\mu$ .

## Results and Discussion

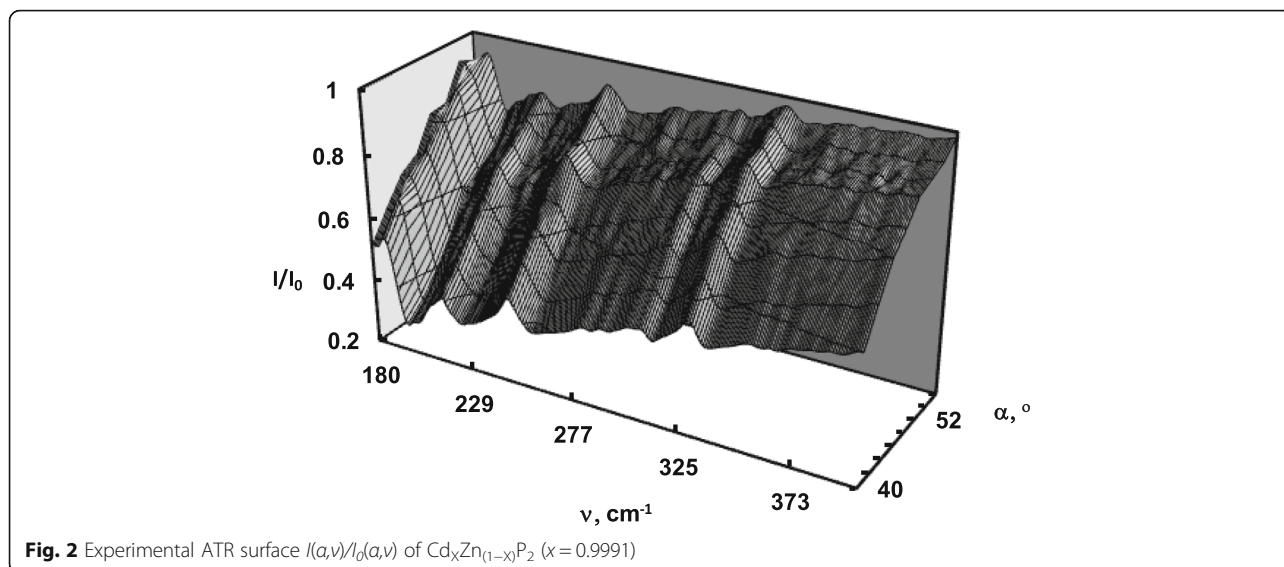
To study the dispersion of SP, the method of ATR was employed. The general principles of the excitation of surface waves by ATR has been proposed and described by Otto in [12] for the surface plasma waves on metals. Figures 1 and 2 represent experimental ATR spectra of  $\text{CdP}_2$  and  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  in form of surfaces  $I(\alpha, \nu)/I_0(\alpha, \nu)$ , which is a three-dimensional presentation of the system's response that depends on the radiation frequency  $\nu$  and angle of its incidence  $\alpha$ . Each surface is formed by eight experimental ATR spectra obtained in the range of  $42 - 55^\circ$  and in the presence of the SP damping and dissipation of

the electromagnetic wave energy the surfaces  $I(\alpha, \nu)/I_0(\alpha, \nu)$  exhibit 7 “canyons” connected with several “passes”. The depth of the “canyon” depends on the gap  $d$  between the ATR semicylinder and sample, radiation frequency  $\nu$ , dielectric permittivity  $\epsilon(\nu)$  of the sample, refractive indexes of the ATR unit and gap. The SP dispersion curves  $\nu_s(k)$  correspond to the “canyons”, i.e., to the set of ATR spectra minima. In order to better show the impact of the doping, we plotted the experimental ATR spectra of  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  ( $x = 1$  and  $x = 0.9991$ ) recorded at  $42^\circ$  in Fig. 3.

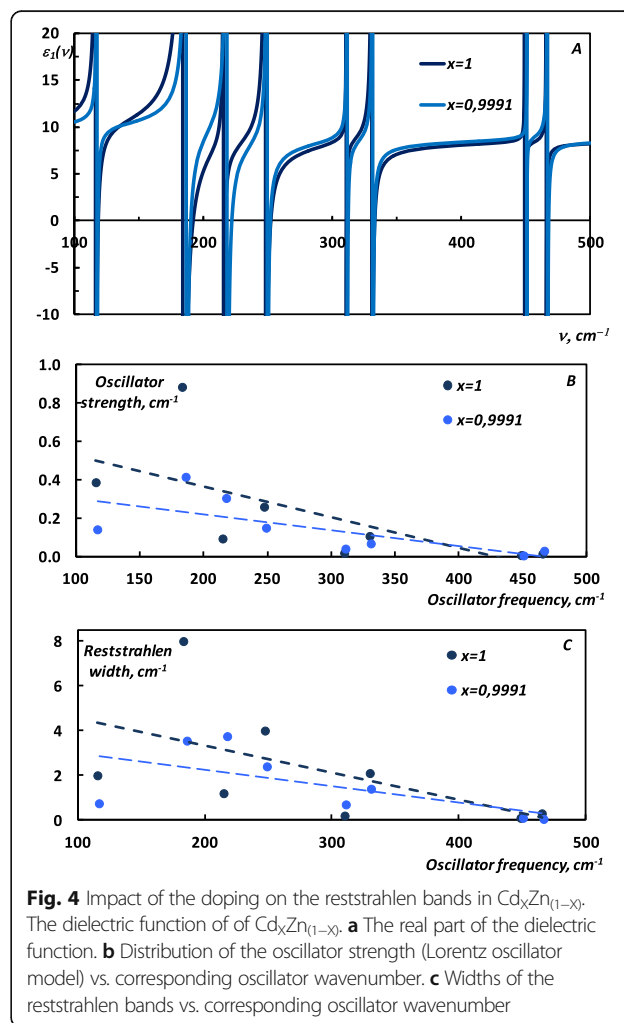
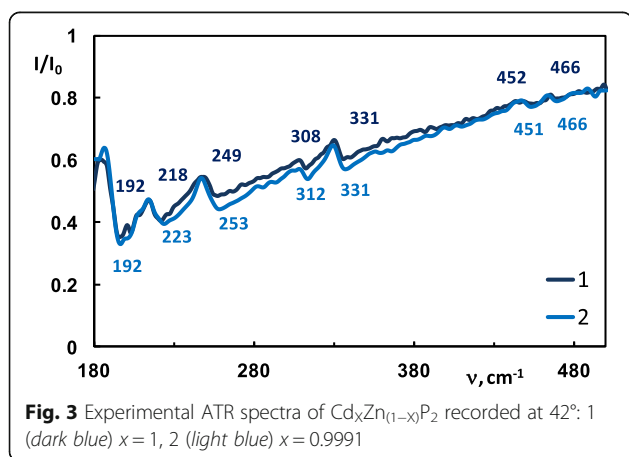
The analysis of the obtained experimental data on SP in  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  we begin with the spectral ranges of their existence. SP propagate along the interface and decay exponentially for directions normal to the interface between two media, one having a negative dielectric permittivity and the other a positive one. Tetragonal  $\beta$ - $\text{CdP}_2$  and  $\alpha$ - $\text{ZnP}_2$  belong to the similar space symmetry group  $P4_12_12 (D_4^+)$  [13], where the vibrational modes have following symmetry types:  $9A_1 + 9A_2 + 9B_1 + 9B_2 + 18E$ , according to the results of the group theoretical analysis [14]. Modes of the symmetry  $A_2(z)$  and  $E(x, y)$  modes are IR active, whereas  $A_1, B_1, B_2, E$  are first-order Raman active. Infrared active  $A_2(z)$  and  $E(x, y)$  modes in  $\text{CdP}_2$  and  $\text{ZnP}_2$  cause occurrence of the several reststrahlen bands in the corresponding dielectric function that have been reported in [3]. In [7], we analysed the effect of the doping of the  $\text{CdP}_2$  single crystal by the  $\text{ZnP}_2$  nanoclusters on the vibrational properties. Due to the similarity of the crystal structure of  $\text{ZnP}_2$  and  $\text{CdP}_2$ , their dielectric functions exhibit similar profile in the IR, exhibiting the similar number and types of the modes. In Fig. 4a, we show the real part of the dielectric function  $\epsilon_1$  (with zero phonon damping) of  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  and  $\text{CdP}_2$  obtained from the reflectance measurements [7]. Replacing Cd by Zn in  $\text{Cd}_x\text{Zn}_{(1-x)}\text{P}_2$  causes evolution of the reststrahlen



**Fig. 1** Experimental ATR surface  $I(\alpha, \nu)/I_0(\alpha, \nu)$  of  $\text{CdP}_2$  ( $x = 1$ )



bands located at lower wavenumbers, that is shown in the Fig. 4: these bands are shifted to the higher wavenumbers, and at the same time they have smaller widths in the comparison to those of the corresponding reststrahlen bands in pure  $CdP_2$ . These findings can be explained in the terms of the electronic polarizability of the vibrating ions and their masses. In tetragonal  $CdP_2$ ,  $ZnP_2$  anion atoms form the zigzag chains which penetrate through the crystal [13]. In [15], the low frequency lattice vibrations have been attributed to the  $Zn(Cd)-P$  and  $Zn(Cd)-Zn(Cd)$  modes, whereas the high frequency peaks were assigned to the internal vibrations of the phosphorus chain. Therefore, in comparison with  $CdP_2$  in  $Cd_xZn_{(1-x)}P_2$  the most changes should occur with the low frequency cation vibrations, whereas the high frequency vibrations of the phosphorus chain should remain mostly unchanged. Difference in the masses of  $Zn$  and  $Cd$  is responsible for the blue shift of the reststrahlen bands that correspond to the cation-cation and cation-anion modes, since different energies are needed for



**Table 1** The position and width of the reststrahlen bands in  $Cd_xZn_{(1-x)}P_2$

No.	$x = 1$		$x = 0.9991$	
	$\nu_1, cm^{-1}$	$\Delta\nu, cm^{-1}$	$\nu_1, cm^{-1}$	$\Delta\nu, cm^{-1}$
1	183.3	8.00	189.65	3.55
2	215.0	1.20	221.55	3.75
3	247.6	4.00	251.5	2.40
4	310.4	0.20	312.0	0.70
5	330.2	2.10	332.5	1.40
6	448.9	0.10	450.95	0.10
7	465.7	0.30	467.05	0.05

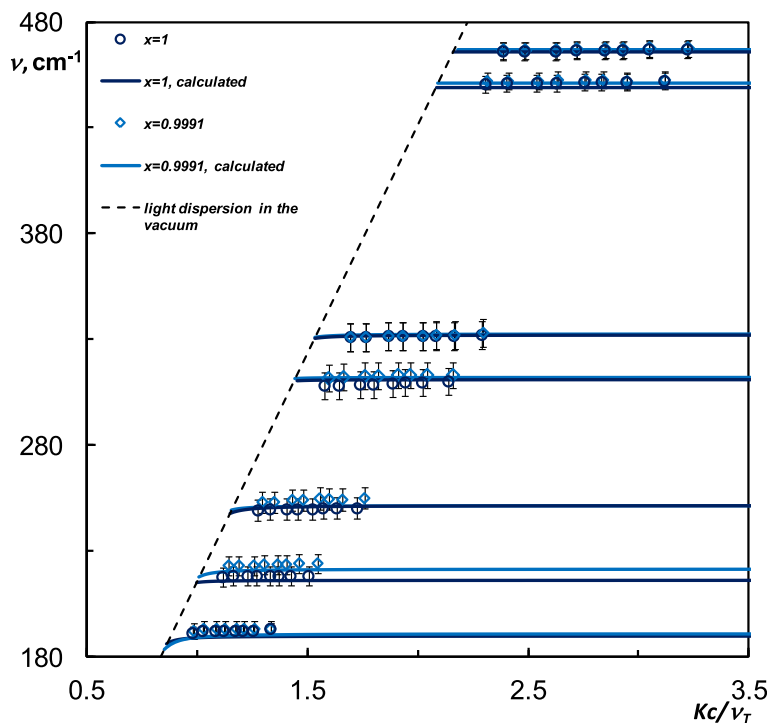
the excitement of the lite Zn and heavy Cd ions. Observed evolution of the widths of the bands can be explained in the terms of the electronic polarizability of the vibrating ions. According to [16], Cd ions exhibit significantly higher polarizability, and therefore, the replacement of the Cd ions by Zn ones, upon forming the  $ZnP_2$ -nanoclusters, reduces the corresponding dipole moment, which we detected in the reduced oscillator strength and the shortening of the spectral width of the corresponding reststrahlen bands, that are presented in Table 1.

The dispersion of the SP  $\nu_s(k)$  in  $CdP_2$  and  $Cd_xZn_{(1-x)}P_2$  has been calculated in the same manner as previously in

[17, 18] with respect to the sample orientation ( $C||y$ ) and using as the input data the discussed above dielectric function of  $CdP_2$  and  $Cd_xZn_{(1-x)}P_2$  within the spectral range of the ATR measurements. According to the Table 1, in both  $CdP_2$  and  $Cd_xZn_{(1-x)}P_2$  calculated dispersion curve  $\nu_s(k)$  of the SP exhibits 7 branches within studied range. From the obtained ATR spectra, we have also distinguished 7 experimental dispersion curves to the SP in each  $CdP_2$  and  $Cd_xZn_{(1-x)}P_2$  within the measured spectral range. However, the minima in the ATR spectra that correspond to the bands between 450 and 467  $cm^{-1}$  were hardly distinguished from the noise due to the weakness of the corresponding modes: the last can also be noticed in the reflectance data [7]. The SP dispersion curves have been evaluated from the ATR spectrum minima in the following way:

$$k = (2\pi\nu/c) n \sin\alpha, \tag{1}$$

here  $\nu$  is the frequency of the ATR spectrum minimum;  $c$  is the speed of light in a vacuum;  $n$  is the refractive index of material of the ATR semicylinder ( $n = 1.72$ , CsI). Thus, we have shown that experimental SP dispersion, shown in dots in Fig. 5, obtained from the ATR spectra is in reasonable agreement with calculated branches.



**Fig. 5** Experimental and calculated dispersion of the SP in  $Cd_xZn_{(1-x)}$ :  $x = 1$ (pure  $CdP_2$ ) and  $x = 0.9991$ (solid solution)

## Conclusions

We applied the spectroscopy of the SP to study the effect of the doping of CdP<sub>2</sub> by ZnP<sub>2</sub> nanoclusters on the properties of the near surface area of Cd<sub>x</sub>Zn<sub>(1-x)</sub>P<sub>2</sub> solid solution. Presence of ZnP<sub>2</sub> nanoclusters in the near surface area of Cd<sub>x</sub>Zn<sub>(1-x)</sub>P<sub>2</sub> causes shift of the reststrahlen bands as well as the shortening of their widths. This finding is confirmed by the observed evolution of the dispersion of the SP in Cd<sub>x</sub>Zn<sub>(1-x)</sub>P<sub>2</sub>. With obtained results, we have shown that the spectroscopy of the SP might be used as a non-destructive method of the property control of the near surface area of Cd<sub>x</sub>Zn<sub>(1-x)</sub>P<sub>2</sub>.

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## Authors' Contributions

TS and VT prepared the samples, KS, TB, and JB performed the measurements. KS, JB, TS, VT, TB, and EV discussed the results. KS analyzed the experimental data and drafted the manuscript. VT and JB helped to draft the manuscript. All authors read and approved the final manuscript.

## Competing Interests

The authors declare that they have no competing interests.

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