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QUANTUM BIEXCITONIC LIQUID IN β-ZnP_2 CRYSTAL

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A phonon-roton dispersion relation is proposed for the elementary excitations of a quantum biexcitonic liquid in semiconductors. The proposed dispersion relation is used as a starting point for a calculation of the photoluminescence spectrum of the liquid and an analysis of its behaviour under variation of the temperature and density of the biexcitonic liquid. The parameters of the dispersion curve of elementary excitations of the quantum biexcitonic liquid are evaluated by fitting the calculated photoluminescence spectrum to the experimental spectrum of the biexcitonic liquid of semiconducting β-ZnP_2 crystals. Experimental studies of how the photoluminescence spectrum of a biexcitonic liquid in β-ZnP_2 depends on the temperature and the intensity of the laser excitation confirm the initial theoretical model. The dependence of the temperature of the crystals on the excitation intensity is measured, and for some of the samples an anomalous dependence is found: the temperature of the crystal decreases as the excitation intensity increases. This effect is probably a consequence of the giant thermal conductivity of the superfluid biexcitonic liquid in β-ZnP_2 crystals.

Key words: biexcitons, quantum biexcitonic liquid, phonon-roton dispersion relation, superfluidity

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I. INTRODUCTION

For a long time the phenomenon of superfluidity was observed exclusively in liquid ^{4}He at temperatures below 2.17 K. It is well known that the dispersion relation for elementary excitations in superfluid He II is characterized by the so-called roton gap. A dispersion relation of this sort was first proposed by Landau [1] and later investigated theoretically by Feynman [2], and it was subsequently confirmed in neutron scattering experiments [3]. Among the Bose liquids, ^{4}He is unique in that it remains liquid at atmospheric pressure down to the lowest temperatures. Other Bose liquids crystallize at temperatures above those at which superfluidity can arise. Crystallization sets in because the energy of the intermolecular interaction is greater than the vibrational energy at temperatures above the temperature of the onset of superfluidity. Since the vibrational energy goes as $\hbar\omega_{\rm vibr} \propto m^{-1/2}$ (m is the mass of the molecule), superfluidity is more likely to arise in liquid molecular hydrogen than in other liquids. However, even in the case of liquid H_2 the energy of the intermolecular interaction is too large, and crystallization sets in before superfluidity as the temperature is lowered.

The analogy between Wannier–Mott excitons in semiconductors and atomic hydrogen is well known. This analogy extends to excitonic molecules (EMs or biexcitons) and to the hydrogen molecule. The problem of Bose condensation and superfluidity in a system of excitons has been very popular in semiconductor physics for the past 20–25 years (see, e. g., Refs. [4]– [6]). The possibility of superfluidity of excitons in a strong magnetic field was pointed out in Ref. [5]. An unusual ballistic solitonlike regime of exciton motion in Cu_2O crystals was observed in Ref. [6]. This effect was interpreted as evidence of superfluidity of Bose-condensed excitons.

Guided by the analogy between excitonic molecules and hydrogen molecules, one can analyze the possibility for superfluidity to arise in such a biexcitonic (molecular) liquid. The existence of a biexcitonic liquid in semiconductors was first considered in Ref. [7]. As we have said, superfluidity is not observed in liquid hydrogen because of the earlier onset of crystallization. However, the effective mass of excitonic molecules is 2–3 orders of magnitude smaller than that of the H_2 molecule, and crystallization of a biexcitonic liquid probably should not occur at all. Therefore, at sufficiently low temperatures a biexcitonic liquid can go into a superfluid state. However, as it turns out, the formation of a biexcitonic liquid itself is extremely problematic. Keldysh [8] and later Brinkman and Rice [9] pointed out two important differences between H_2 molecules and EMs in typical semiconductors. First, since the effective masses of the electron and hole are often of the same order, the binding energy of the excitonic molecule, measured in units of the binding energy of the exciton (atom), should be much less than 0.35 for the hydrogen molecule. Secondly, the contribution of the energy of zero-point motion is considerably larger in a system of biexcitons because of the small mass of a biexciton. For these two reasons, as experiments have shown, in typical semiconductors (Si, Ge, and a number of others) at high excitation intensities an electron-hole Fermi liquid is formed. One, therefore, expects that the formation of a biexcitonic Bose liquid can occur only in crystals in which the effective masses of the electron and hole are sufficiently different. Furthermore, the mass of the EM should be sufficiently large that the contribution of the zero-point motion is sufficiently small and it becomes possible for a molecular liquid to form. At the same time, the mass of the EM must be small enough that "early" crystallization cannot occur.

Crystals of monoclinic zinc diphosphide (β-ZnP_2)

meet the stated requirements. This crystal is characterized by an appreciable difference of the electron and hole effective masses ($\sigma = m_e/m_h = 0.06$), a rather large value of the translational mass of the biexciton $m_{\rm bex} = 3m_0$ (m_0 is the free electron mass), and a very strong anisotropy of the effective masses of the carriers. For example, the anisotropy parameter $\gamma = \mu_{\|}/\mu_{\perp}$ is equal to 0.19 ($\mu_{\|}$ and $\mu_{\perp}$ are the values of the reduced masses of an exciton in the directions parallel to and perpendicular to the Z (c) axis of the crystal). As we know, the anisotropy leads to an increase in the binding energy of free electron-hole complexes, i. e., excitons, biexcitons, and their condensates. Therefore, the excitonic molecule in β-ZnP$_2$ has a rather high binding energy $E^b_{\rm bex} = 6.7$ meV $= 0.15E^b_{\rm ex}$.

The excitonic state with the lowest energy in this crystal is the dipole-forbidden $1S$ state of the orthoexciton [10]. This makes it rather easy to create an appreciable concentration of excitons and, hence, biexcitons under laser excitation. Studies by the authors have shown that the condensation of biexcitons in β-ZnP$_2$ crystals occurs via a hydrogenlike scenario, i. e., unlike the case of typical semiconductors, a liquid of the molecular (insulator) type forms in them. In the photoluminescence (PL) spectrum of these crystals one observes the so-called C line, which is due to two-photon annihilation of biexcitions condensed into a molecular (insulator) liquid [11–13]. Note, that at two-photon annihilation there is no recoil particle that could take an appreciable part of the momentum of the annihilating EM. For this reason, since the photon momentum is very small, momentum conservation allows two-photon decay only for an EM with $k \approx 0$, i. e., the two-photon PL line should be very narrow [14]. In two-electron (one-photon) transitions, in which only one exciton of a molecule annihilates, the second, surviving exciton can take an arbitrary quasimomentum, i. e., the one-photon PL lines are rather wide. This makes it possible to distinguish the two-photon PL lines of free biexcitons and of a biexcitonic liquid, unlike the case of the one-photon PL lines. In Refs. [12] and [13] the phase diagram of a biexcitonic liquid was measured and its critical parameters were determined: $T_C = 4.9$ K, $n_{{\rm bex},C} = 4.1 \times 10^{18}$ cm^{-3} ($r_{{\rm bex},C} \approx 63$ Å $= 4.2a_{\rm ex}$, where $a_{\rm ex}$ is the excitonic Bohr radius).

In this paper we propose a model for the quantum biexcitonic Bose liquid and calculate its emission spectrum. In the framework of this model we analyze the experimentally observed features of the fine structure of the emission line of a biexcitonic liquid in β-ZnP$_2$ (the C line) as the temperature and the intensity of the laser excitation of the crystal are varied.

II. DISPERSION RELATION FOR ELEMENTARY EXCITATIONS OF A QUANTUM BIEXCITONIC LIQUID

Thus we assume that the biexcitonic liquid does not crystallize down to the temperatures at which quantum effects become important. What sorts of elementary excitations can exist in a quantum biexcitonic Bose liquid? It is logical to assume that, first, there are acoustic phonons. Their dispersion relation is given as

$$E(k) = \hbar u k\,, \tag{1}$$

where u is the sound velocity, and k is the wave vector. Second, we assume that owing to the intermolecular interaction in the liquid a collectivization of the intramolecular excitations can occur in it. Since the lowest-energy excited state of an excitonic molecule is a rotational state [15], these collectivized molecular excitations can be rotational excitations of the molecules. Here, following Landau [1], these collectivized excitations/quasiparticles will be called rotons. Rotons in a biexcitonic (molecular) liquid can be regarded as molecular Frenkel excitons. The excitation energy of the molecule in the presence of phase correlation between the molecules in the liquid can be written as

$$\Delta E = \Delta E_0 + D + 2M\cos[(k - k'_0)a)]\,, \tag{2}$$

where ΔE_0 is the excitation energy of a free molecule, D is the change of the interaction energy of a given molecule with its neighbours under its excitation, M is the matrix element for the transfer of the energy of excitation from the excited molecule to a neighbour being in the ground state, a is the average distance between these molecules, and k is the wave vector of a Frenkel exciton, i. e., in our case the roton. The last term in Eq. (2) describes the dispersion relation of rotons and is physically meaningful for $|\Delta k| = |k - k'_0| \le \pi/2a$. Thus the photon-roton dispersion relation for elementary excitations of a biexcitonic liquid can be written as

$$\begin{gathered} E(k) = \hbar u k \text{ at } 0 \le k < k'_0 - \pi/2a \\ \text{and } k > k'_0 + \pi/2a\,; \\ E(k) = \hbar u k - \gamma\cos[(k - k'_0)a)] \\ \text{at } k'_0 - \pi/2a \le k \le k'_0 + \pi/2a\,, \end{gathered} \tag{3}$$

where $\gamma = -2M$. For small $|\Delta k|$ the second relation of system (3) can be written in the form

$$E_r(k) = \Delta + \frac{\hbar^2(k - k_0)^2}{2m_r}\,. \tag{4}$$

Equation (4) is exactly the same as the equation proposed by Landau [1] for describing the dispersion relation of rotons in superfluid He II. Thus our choice of the term "roton" is not arbitrary but is based on the similarity of the dispersion relations of rotons in helium and the collectivized molecular excitations of a biexcitonic liquid. In Eq. (4) we have introduced the following notation: $m_r = -\hbar^2/2Ma^2$ is the roton effective mass, $k_0 = k'_0 - m_r u/\hbar$ is the wave vector corresponding to the roton minimum of the dispersion relation, and $\Delta = \hbar u k_0 + 2M + m_r u^2/2$ is the energy gap in the spectrum of elementary excitations of the biexcitonic liquid.

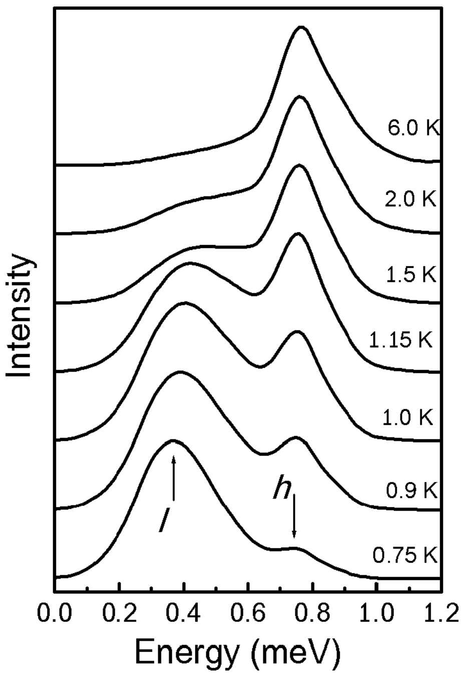

Fig. 1. Evolution with temperature of the calculated photoluminescence spectrum of a quantum biexcitonic liquid with a phonon-roton dispersion relation for the elementary excitations. The arrow labeled l indicates the low-energy (l) component of the spectrum, and the arrow h the high-energy (h) component.

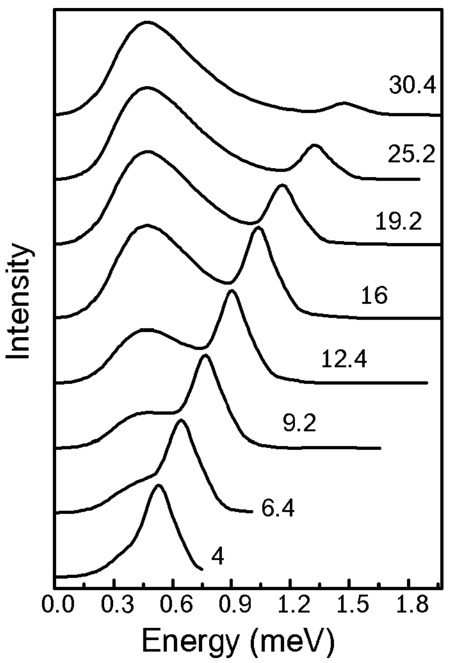

Fig. 2. Evolution of the theoretical PL spectrum of a quantum biexcitonic liquid under variation of the square of the excitation intensity (density of the liquid): $n \propto I_{\text{ex}}^2$. The curves are labeled with the value of I_{ex}^2 in arbitrary units.

Starting from the dispersion relation (3) for a quantum biexcitonic liquid, let us calculate the PL spectrum for such a liquid. The spectrum we are looking for can be obtained by convolution of the slit function and the function $I(E) = I_0\rho(E)f(E)$, where $I_0 = \text{const}$, $\rho(E) = \rho_0 k^2(E)(dk(E)/dE)$ is the density of states of the liquid, which is determined from the dispersion relation for the elementary excitations ($\rho_0 = \text{const}$); $f(E) = 1/[\exp(E/k_BT) - 1]$ is the distribution function for the excitations/quasiparticles of the liquid (the Bose–Einstein distribution function). The zero of energy E is taken as the value corresponding to the radiative transition from the state with $k = 0$. For the parameters of the dispersion curve we used the values obtained from a best fit of the calculated luminescence spectrum to the experimental PL spectrum of a biexcitonic liquid, recorded for a β-ZnP_2 crystal of high purity. Figures 1 and 2 show an evolution of the calculated PL spectra of a quantum biexcitonic liquid at variation of temperature and density of liquid, respectively (the density of the biexcitonic liquid is proportional to I_{exc}^2). It is seen that the PL spectrum of a biexcitonic liquid should have a two-component structure. In the proposed model it is assumed that the shape and parameters of the dispersion curve do not depend on temperature and depend only on the density of the liquid . The density of the liquid influences the shape of the dispersion curve and, through it, the shape of the PL spectrum. We used the following proportionalities relating the parameters of the dispersion curve and the density of the liquid (which is proportional to the square of the excitation intensity): average intermolecular distance $a \propto n^{-1/3} \propto I_{\text{ex}}^{-2/3}$, sound velocity $u \propto n^{1/2} \propto I_{\text{exc}}$, $k_0' a = \text{const}$, and the modulus of the matrix element for the excitation transfer between molecules of the liquid $|M| \propto a^{-3} \propto I_{\text{exc}}^2$.

Concluding this Section we must mention the following. A short-range order should be established in the system of biexcitons due to the substantial interaction between them; however, there is apparently no long-range order. The presence of short-range order ensures that relation (2) will apply at least in a qualitative way.

III. BIEXCITONIC LIQUID IN β-ZNP_2 CRYSTALS. EXPERIMENTAL RESULTS AND DISCUSSION

At excitation intensities above 1 kW/cm^2 and temperatures below 5 K the PL spectrum of β-ZnP_2 crystals, as we have said, contains an emission line of the biexcitonic liquid (the C line, henceforth called the C spectrum). As we see from Figs. 3, 4, and 5, the C spectrum has a two-component form, as was predicted by the model set forth above. Using the dispersion relation of elementary excitations of a biexcitonic liquid (3) we fit the experimental PL spectrum of the biexcitonic liquid (Fig. 3), which was obtained for a sample of high purity (excitation energy 3 kW/cm^2). This made it possible to determine the parameters of the dispersion curve of the elementary excitations: $\Delta = 0.49$ meV, $k_0 = 9.8\times10^6$ cm^{-1}, $u = 1.4 \times 10^5$ cm/s, and $m_r = 2.2m_0$ (m_0 is the free electron mass), and also the value of the intermolecular distance in the liquid $a = 92$ Å $= 6.1a_{\rm ex}$ and the temperature of the crystal at the point of excitation, $T = 1.5$ K. The values obtained are physically reasonable, the fact which, in our view, tends to confirm that the proposed theoretical model is correct. Further evidence of this is the good agreement of the experimental and theoretical spectra, in view of the approximate, model character of the dispersion curve given by Eqs. (3).

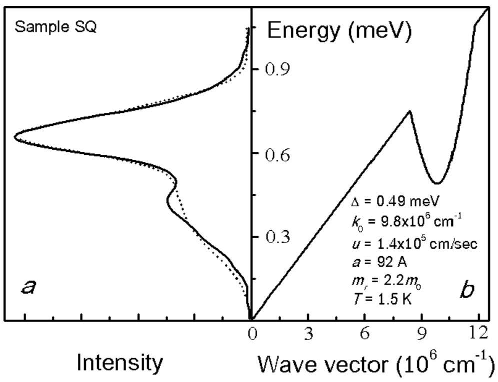

Fig. 3. Experimental PL spectrum of a biexcitonic liquid in a β-ZnP_2 crystal (solid curve) and its approximation by the theoretical spectrum (dashed curve) (a); the dispersion curve for the elementary excitations of the quantum biexcitonic liquid with the parameters obtained by fitting the theoretical PL spectrum to the experimental spectrum (b). Excitation intensity is 3 kW/cm^2.

The evolution of the shape of the C spectrum under variation of temperature and of the square of the excitation intensity are shown in Figs. 4, and 5. The behaviour of the experimental spectrum under variation of temperature (Fig. 4) is similar to that of the theoretical spectrum (Fig. 1). Analysis of the C spectrum under variation of the excitation intensity is made difficult by the fact that simultaneously with the variation of excitation intensity there is also a variation of temperature, which has a definite effect on the shape of the spectrum. We can conclude that the change in the C spectrum at moderate levels of excitation is probably due mainly to the influence of temperature (the rise in temperature with increasing $I_{\rm exc}$), while at higher excitation intensities the evolution of the shape of the C spectrum occurs mainly on account of the increase in the density of the liquid with increasing $I_{\rm exc}$. What we have said agrees with the intensity dependence of the temperature of the crystal at the point of excitation, shown in Fig. 6. Thus the experiment is described by the theory in a completely satisfactory way. The shape of the C spectrum can differ substantially for different samples. This is due to the fact that at the same values of the excitation intensity and crystal temperature, a liquid of higher density should arise in more pure samples than in less pure samples. Consequently, the shape of the PL spectrum of the liquid varies with its density.

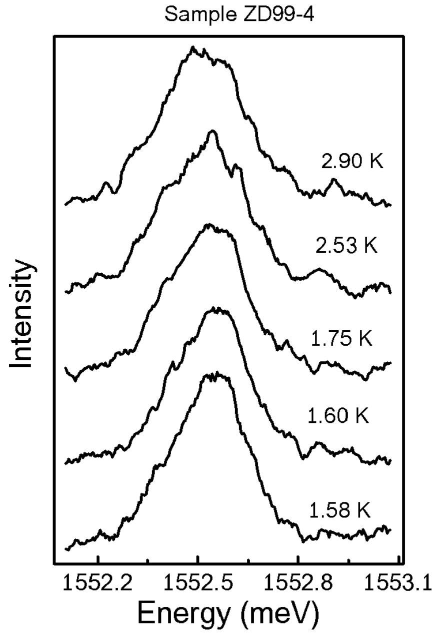

Fig. 4. Evolution of the experimental PL spectrum of a biexcitonic liquid in a β-ZnP_2 crystal under variation of temperature of the sample at the point of excitation. Excitation intensity is 4.8 kW/cm^2.

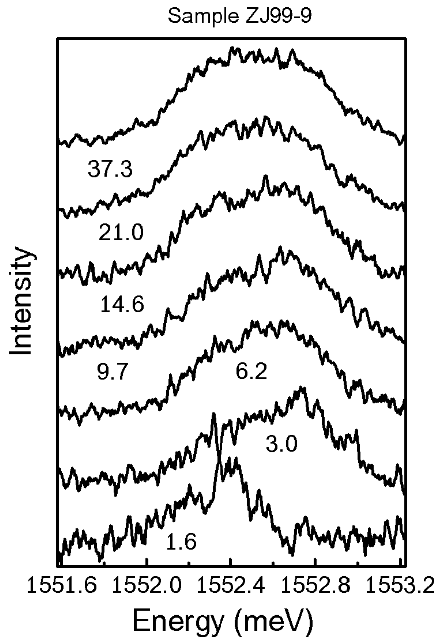

Fig. 5. Evolution of the experimental PL spectrum of a biexcitonic liquid in a β-ZnP_2 crystal under variation of the square of the excitation intensity. The curves are labeled by the value of $I^2_{\rm exc}$ in (kW/cm^2)^2.

The results presented above suggest that a quantum biexcitonic liquid characterized by a phonon-roton dispersion relation for the elementary excitations can form in β-ZnP_2 crystals under certain conditions. This sort of dispersion relation, as we know, is evidence that superfluidity can arise in a Bose liquid, in particular, in liquid ^{4}He. Is it possible that superfluidity can arise in a biexcitonic liquid in a β-ZnP_2 crystal? To answer this question we performed the following experiments. For some of the samples (Fig. 6) we studied the temperature of the crystal at the point of excitation as a function of the intensity of the excitation.

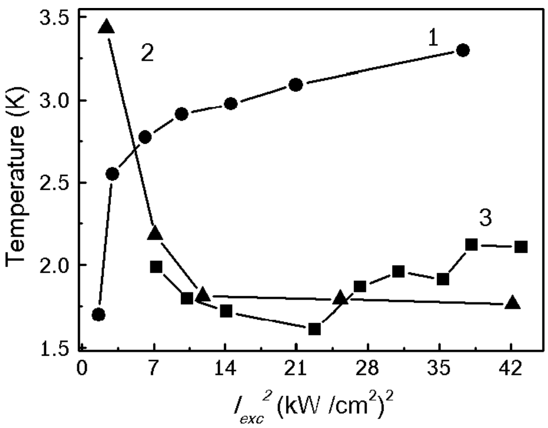

Fig. 6. Temperature of the crystal versus the square of the excitation energy for different samples: ZJ09-9 (*1*), ZJ09-14 (*2*), and ZD99-1 (*3*).

The normal situation is for the temperature of the crystal to increase with increasing of the excitation intensity. Besides the normal monotonically increasing behaviour of $T(I_{\rm ex}^2)$ (curve *1*), for several samples we also obtained anomalous $T(I_{\rm ex}^2)$ curves: decreasing (curve *2*) or nonmonotonic (curve *3*). We think that the anomalous $T(I_{\rm ex}^2)$ dependences can be explained by an anomalously large (giant) thermal conductivity, which accompanies the appearance of the superfluid (s) component in a quantum liquid below the superfluid transition. Such an effect is well known for superfluid He II. We propose the following explanation for the anomalous behaviours observed. At a certain excitation intensity the density of the liquid reaches values sufficient for a transition of the liquid to the superfluid state. Upon further increase in $I_{\rm exc}$ the density of the liquid increases, with the result that the temperature of the superfluid transition increases and, with it, the fraction of the s component. This can increase the thermal conductivity, i. e., the thermal energy should be removed more efficiently from the excitation region of the crystal, and so the temperature of the crystal should decrease with increasing excitation intensity. Apparently those crystals with a monotonically decreasing $T(I_{\rm ex}^2)$ curve (curve *2* in Fig. 6) are the purest and most perfect: they have a low concentration of lattice defects, and therefore a biexcitonic liquid is formed in them with a sufficiently high density for the onset of superfluidity and the corresponding giant thermal conductivity. Those crystals with a nonmonotonic $T(I_{\rm ex}^2)$ curve (curve *3* in Fig. 6) would be less pure. The liquid formed in them is of a lower density but is nevertheless sufficient for the appearance of the s component. However, this component represents a smaller fraction than in the perfect crystals, and the giant thermal conductivity provides a sufficiently effective heat removal only up to certain values of the incoming laser power. When the power is increased further, the temperature of the crystal begins to grow. In those crystals with a monotonically increasing $T(I_{\rm ex}^2)$ dependence (curve *1* in Fig. 6) the concentration of defects is rather high, and therefore the density of the liquid in them does not reach the values necessary for a transition to the superfluid state and the resulting onset of giant thermal conductivity. As a result, the temperature of the crystal at the point of excitation increases with increasing excitation intensity.

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КВАНТОВА БІЕКСИТОННА РІДИНА У КРИСТАЛІ β-ZnP_2

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Запропоновано фотон-ротонне дисперсійне співвідношення для елементарних збуджень квантової біекситонної рідини в напівпровідниках. Це співвідношення використано як вихідний пункт для обчислення спектра фотолюмінісценції рідини й аналізу його поведінки при зміні температури та густини біекситонної рідини. Параметри дисперсійної кривої для елементарних збуджень для квантової біекситонної рідини оцінено при порівнянні обчисленого спектра фотолюмінісценції й експериментального спектра біекситонної рідини напівпровідникового кристала β-ZnP_2. Експериментальні дослідження залежности спектра фотолюмінісценції біекситонної рідини у β-ZnP_2 від температури й інтенсивности лазерного збудження підтверджують вихідну теоретичну модель. Виміряно залежність температури кристала від інтенсивности збудження і для кількох зразків знайдено аномальну залежність: температура кристала зменшується, коли інтенсивність збудження зростає. Цей ефект, мабуть, є наслідком гігантської термічної провідности надплинної біекситонної рідини у кристалі β–ZnP_2.