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PECULIARITIES OF EXCITON CONDENSED PHASE DEVELOPMENT

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A theory of exciton condensed phase development is presented taking into account the mutual influence of exciton drops and inhomogeneous of exciton density distribution in vicinity of a drop. For solution of the problem the Fokker-Planck equation is applied. The distribution functions of the both the radius of drops and their concentration are obtained as function of exciton production rate and other parameters of crystal. With increasing the pumping the mean radius of drops increases faster than mean distance between drops. The both values depend significantly on diffusion coefficient. The radius distribution function becomes broader in vicinity of threshold of exciton condescend phase development.

Keywords: exciton; high intensity; drops; distribution function

INTRODUCTION

There were many attempt to observe exciton condensed phase. Due to attractive interaction between excitons the condensed phase of exciton (exciton liquid) may be created. Stirring problem is the problem of Bose-Einstain condensation of excitons [1,2] with its interesting physical consequences: superfluidity, narrowing of optical bands and others. But usually electron-electron correlation energies in condensed phase are larger than energy of interaction between excitons and consequently excitons lose their individuality and well known and well good studied state of electron-hole liquid is created [3]. The creation of electron-hole liquid phase was observed and studied in germanium, silicon and other materials [4–8].

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However there are several examples of inorganic crystals in which the exciton binding energy is high and excitons save their individuality at large density. Several groups have reported the observation of Bose-Einstain distribution of excitons in CU_2O when using intense pulsed photoexcitation [2]. Anomalous propagation of excitonic packet in CU_2O has been attributed by authors [9] to superfluidity. But there is active discussion of these results with another explanation with phonon – wind effect [10] and due to Auger decay processes, heterogeneous distribution of exciton gas [11]. So the observation of Bose-Einstain condensation is not conformed in bulk materials.

Recently convincing arguments about existence of biexciton condensed phases were obtained in the semiconductor ZnP_2 [12–13]. In this crystal the excitons have intermediate radius value between its values in organic and semiconductor crystals and large values of effective mass and binding energy. These facts promote the exciton condensed phase development. The authors [12–13] observed very narrow line which arisen at threshold value of pumping in both cases: steady-state and pulse light irradiation. The phase diagram obtained in the articles contains the region where gas and condensed phases coexistence. So in this system the drops of condensed phase should be observed similar to the drops of electron-hole liquid in germanium and silicon.

In organic crystal the Frenkel excitons save their individuality even at large density because in organic crystal the ionized levels with departed electron and hole are situated significantly higher than exciton level. However since the exciton radius in organic crystals is small the space distance between excitons in condensed phase should have order of period of crystal lattice. At such conditions the processes of exciton-exciton annihilation become very intensive that hamper the creation of condensed phase. For this reason in organic crystal the condensed exciton phase was not observed so far. The exciton-exciton annihilation may be suppressed for triplet excitons by strong magnetic field and appearance of exciton condensed phase may be realized [14].

The dependence of the number of drops and the radius distribution function of drops on intensity of pumping and other parameters of system is investigated in the presented paper. We have solved the self-consisted problem in which the number of drops depends on exciton density and exciton density is determined by the number of drops. For electron-hole liquid the radius distribution function of drops was studied in [15,16]. Under consideration on exciton liquid in comparison with [15,16] we took into account the heterogeneous distribution of exciton density in vicinity of drop and back influence of density of drops on exciton density. It allows to us to determine the density of drops.

MODEL UNDER CONSIDERATION. SOLUTION OF FOKKER-PLANCK EQUATION

We shall investigate the crystal in which at high exciton density the exciton drops arise. Since the drops absorb the excitons the distribution of excitons is heterogeneous in vicinity of drops. We shall describe the distribution of the excitons in space by the density $c(\mathbf{r})$. It will be suggested that exciton density satisfy diffusion equation. In such way we may describe the system on the distances greater than free path of exciton. So we suggest that radiuses of drops exceed significantly the free path.

The size of drops is determined by four processes: capture of the excitons from environment, escape of the exciton from the drop, creating of excitons by external irradiation and their decay as the result of light emission and different processes of destruction. Lets f_n is the distribution function with respect to n – number of excitons in drop. Taking into account the above mentioned processes the kinetic equation for distribution function may be presented in the following form

$$\frac{\partial f_n}{\partial t} = -j_{n+1} + j_n, \tag{1}$$

where j_n is the probability current

$$\begin{aligned} j_n = {} & (4\pi R_n^2 c(R_{n-1}) W_{fi}(R_{n-1}) + (n-1)v_0 K) f_{n-1} \\ & - (4\pi R_n^2 c_i W_{if}(R_n) + n/\tau) f_n \end{aligned} \tag{2}$$

R_n is the radius of the drop with n excitons, $c(R_n)$ and c_i are the concentrations of excitons on the surface of the drop and inside of the drop respectively ($c_i = 1/v_0, v_0$ is the volume per single exciton inside of a drop), $W_{fi}(R_n)$ and $W_{if}(R_n)$ are the probability of particle transition from outside of drop to inside of drop and back per unit area, K is the creation rate – the number of excitons created in unit volume in unit time, τ is the lifetime of exciton.

As result of detail balance principle the following condition between probabilities of transition $W_{fi}(R_n)$ and $W_{if}(R_n)$ takes place

$$\frac{W_{if}(R)}{W_{fi}(R)} = \frac{W_{if}(\infty)}{W_{fi}(\infty)} \exp\left(\frac{\alpha}{R}\right), \tag{3}$$

where $W_{fi}(\infty)$ and $W_{if}(\infty)$ are the probability in the case of plain boundary between phases, $W_{fi}(\infty)/W_{if}(\infty) = c_i/c_\infty$, c_∞ is the equilibrium concentration of excitons for plane boundary between condensed and gas phases, $c_\infty = D_s \exp(-\varphi/\kappa T)$, φ is the condensation energy per a exciton, $D_s = \gamma(m^* \kappa T/2\pi\hbar^2)^{2/3}$, m^* is the effective exciton mass, γ is the degeneracy of the exciton state, $\alpha/R = (2v_0\sigma)/(\kappa T R)$ is the surface energy

connected with changing the number of particles on unity, σ is the surface tension.

Further we introduce the radius distribution function $f(R) = f_n dn/dR = 4\pi R^2 f_n/v_0$. In the case of large number of excitons in drops the kinetic Eq. (1) for $f(R)$ may be transformed to the following Fokker – Planck equation

$$\frac{\partial f(\tilde{R})}{\partial t} = -\frac{\partial}{\partial \tilde{R}} A(\tilde{R}) f(\tilde{R}) + \frac{\partial}{\partial \tilde{R}} B(\tilde{R}) \frac{\partial f(\tilde{R})}{\partial(\tilde{R})}, \tag{4}$$

where

$$A(\tilde{R}) = \left(v(\tilde{c}(\tilde{R}) - \tilde{c}_\infty e^{\alpha/\tilde{R}}) + \frac{\tilde{R}}{3}(c(\tilde{R}) - 1) \right) \frac{1}{\tau}, \tag{5}$$

$$B(\tilde{R}) = \left(v(\tilde{c}(\tilde{R}) + \tilde{c}_\infty e^{\alpha/\tilde{R}}) + \frac{\tilde{R}}{3}(c(\tilde{R}) + 1) \right) \frac{1}{8\pi \tilde{R}\tau} \tag{6}$$

We have introduced the dimensionless variables

$$\tilde{c}(R) = c(R)v_0, \; W_{fi}\tau v^{1/3} = v, \tilde{R} = Rv^{-1/3}. \tag{7}$$

In stationary case the solution of the Eq. (4) equals

$$f(\tilde{R}) = f_0 \exp\left(\int_0^{\tilde{R}} A(\tilde{R})/B(\tilde{R})\, d\tilde{R} \right). \tag{8}$$

The influence of other drops on considered drop is located in the value of $c(\tilde{R})$. To look for this value we should solve the diffusion equation for excitons in presence of many drops.

SPACE DISTRIBUTION OF EXCITONS IN CRYSTAL. NUMBER OF DROPS

The diffusion equation for exciton concentration equals

$$\frac{\partial c}{\partial t} = D\Delta c - \frac{c}{\tau} + K, \tag{9}$$

where D is the diffusion coefficient.

The steady-state solution of Eq. (9) has the form

$$c(\mathbf{r}) = c_K + \sum_i a_i \frac{\exp(-|\mathbf{r} - \mathbf{r_i}|/l_D)}{|\mathbf{r} - \mathbf{r_i}|}, \tag{10}$$

where $\mathbf{r}_i$ is the position of i-th drop, $l_D = \sqrt{D\tau}$ is the diffusion length, $c_K = K\tau$, a_i is the constant values which are determined by boundary conditions on every drop. In vicinity of some drop the exciton concentration field depends on a considered drop and all other drops. Because of the large distance between drops the concentration field created by other drops in the place of a considered drop may be suggested as uniform. For example let us consider concentration field in vicinity of the drop with $\mathbf{r_i} = 0$. We shall designate this drop by $i = 0$. Then we have

$$c(\mathbf{r}) = c_0 + a_0 \frac{\exp(-r/l_D)}{r}, \tag{11}$$

where

$$c_0 = c_K + \sum_{i \neq 0} a_i \frac{\exp(-|\mathbf{r_i}|/l_D)}{r_i}. \tag{12}$$

At large value of diffusion length l_D the term of the sum in (12) decreases very slowly with increasing distance r_i between i-th drop and considered drop. It means that many drops give a contribution in distribution of concentration in vicinity of drop with $\mathbf{r_i} = 0$. Under these conditions we may carry out a_i from the sum at mean value $\bar{a}$ and change the sum by integral. As the result we obtain

$$c_0 = c_K + 4\pi \bar{a} n \, l_D^2, \tag{13}$$

where n is the concentration of drops $n = N/V$, N and V are the total number of the drops and volume of system respectively.

The second term in (13) describe the influence of the drops on exciton density. As we shall see the value $\bar{a}$ is negative, and presence of drops leads to decreasing the exciton density.

To obtain the boundary condition for concentration on the surface of drop let us consider the conversation particle law on surface of the drop

$$4\pi R^2 D \frac{\partial c}{\partial R} = 4\pi R^2 (W_{fi} c(R) - W_{if} c_i). \tag{14}$$

From (3), (11) and (14) the condition follows

$$a_0 = -\frac{W_{fi}(c_0 - c_\infty \exp(\alpha/R))R^2}{D + W_{fi}R}. \tag{15}$$

If there is the very fast exchange by excitons between a drop and environment ($W_{fi}R >> D$) we have

$$a_0 = -(c_0 - c_\infty \exp(\alpha/R))R. \tag{16}$$

Such approximation is used very often in the theory of phase transition.

In general case for determination of a_0 from (15) we should know To obtain $\bar{a}$ let us look for the mean value of the left and right parts of the Eq. (15). Also we shall suggest that the radius distribution function has sharp maximum at $R = \bar{R}$. Afterwards we shall conform this approximation. As the result we obtain

$$\bar{a} = -\frac{W_{fi}(c_0 - c_\infty \exp(\alpha/\bar{R}))}{D + W_{fi}\bar{R} + 4\pi\, W_{fi} N \bar{R}^2 l_D^2}\bar{R}^2. \tag{17}$$

Therefore, the exciton concentration on the surface of the drop is equal

$$c(R) = c_K + \frac{a_0}{R} + 4\pi\,\bar{a} n l_D, \tag{18}$$

where $a_0, \bar{a}$ are determined by formulae (13), (15) and (17).

After substitution of $c(R)$ in (5), (6) we obtain the expression for radius distribution function (8) at fixed value of concentration of the drops n. Further the distribution function will be presented in dimensionless units, but mark "tilde" is omitted

$$f = f_0 \exp(-F(n, R), \tag{19}$$

where

$$F(n,R) = 4\pi \int_0^R \frac{(l_D^2 v(c_0 - c_\infty \exp(\alpha/R))/3 + R(c-1)(l_D^2 + vR))R^2}{(vc_\infty \exp(\alpha/R) + R(c+1)/6)(l_D^2 + vR) + l_D^2 v(c_0 - c_\infty \exp(\alpha/R))/2}\, dR \tag{20}$$

$$c_0 - c_\infty \exp(\alpha/R) = \frac{(l_D + v\bar{R})(c - c_\infty \exp(\alpha/R)) + 4\pi v N c_\infty (\exp(\alpha/\bar{R}) - \exp(\alpha/R))\bar{R}^2 l_D^2}{l_D^2 + v\bar{R} + 4\pi v N l_D^2 \bar{R}^2} \tag{21}$$

The probability for system to have N drops with radiuses $R_1, R_2, \ldots, R_N$ is given by

$$W(N, R_1, R_2, \ldots, R_N) \approx \exp\left(-\sum_i F_n(R_i)\right). \tag{22}$$

After integrating over the radiuses of the drops we obtain the probability for system to have N drops

$$W(N) = W_0 \exp(-\Phi(N)), \tag{23}$$

where

$$\Phi(N) = -N \ln z\left(\frac{N}{V}\right), \qquad z\left(\frac{N}{V}\right) = \int_0^\infty \exp\left(-F\left(\frac{N}{V}, R\right)\right) dR \tag{24}$$

The most probable concentration of the drops is determined by the condition

$$\frac{d}{dN}\Phi(N) = 0. \tag{25}$$

In vicinity of maximum radius distribution function the function $F(n, R)$ can be expand in a power series in $(R - \bar{R})$

$$F(n, R) = F(n, \bar{R}) + b(R - \bar{R})^2 + \cdots \tag{26}$$

In this case

$$\Phi(N) = N\left(F\left(\frac{N}{V}, \bar{R}\right) - \frac{1}{2}\ln(\pi/b)\right). \tag{27}$$

Later using numerical calculation we shall show that (27) is good approximation.

CALCULATIONS AND DISCUSSION

Since drops derive excitons from environment two drops can not be situated close one to another because exciton resources of environment are created by external irradiation and are restricted. They can not be situated far one from another since in this case there is high probability of appearance of a new drop in the space between them. So there is a spatial correlation in position of exciton drops. As the result the dependence $\Phi(N)$ has minimum at some value of N. The most probable state is the state which corresponds to minimum of $\Phi(N)$ as function of N (or n at fixed volume). We have made the analysis of properties of crystal with drops in wide range of the values of external and internal parameters numerically solving the Eq. (25). The pumping is described by the value of $c_K = K\tau$ i.e. by the concentration created by pumping in absence of drops. The main results are following.

The drops appear if the pumping is greater than some critical value which depends on surface energy, temperature and the lifetime of exciton.

The radius of drops and mean distance between them ($d = n^{1/3}$) growth with increasing the pumping. But the radius rises significantly faster than distance between drops (see Figs. 1 and 2). (The results are presented in demensional units. The unit of length is the distance between particles in

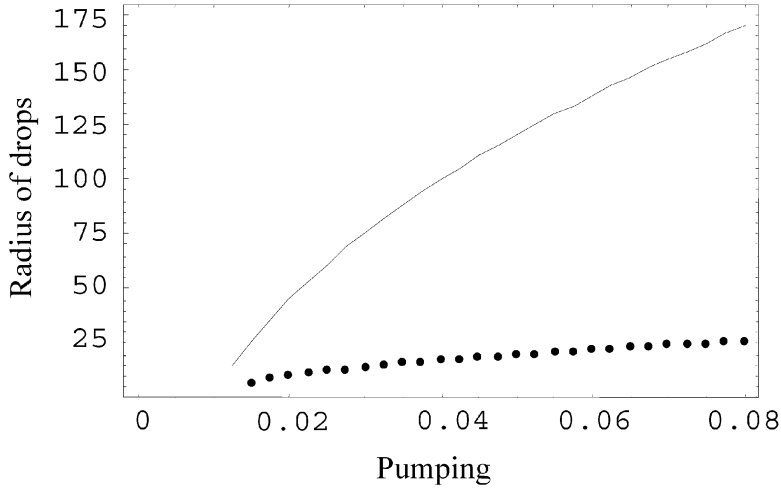

FIGURE 1 The dependence of mean radius ($\bar{R}$) on pumping (c_K). The parameters of system are following: $c_\infty = 0.01$, $\alpha = 0.1$, $v = 4000$, $l_D = 100$ (dashed line), $l_D = 1000$ (solid line).

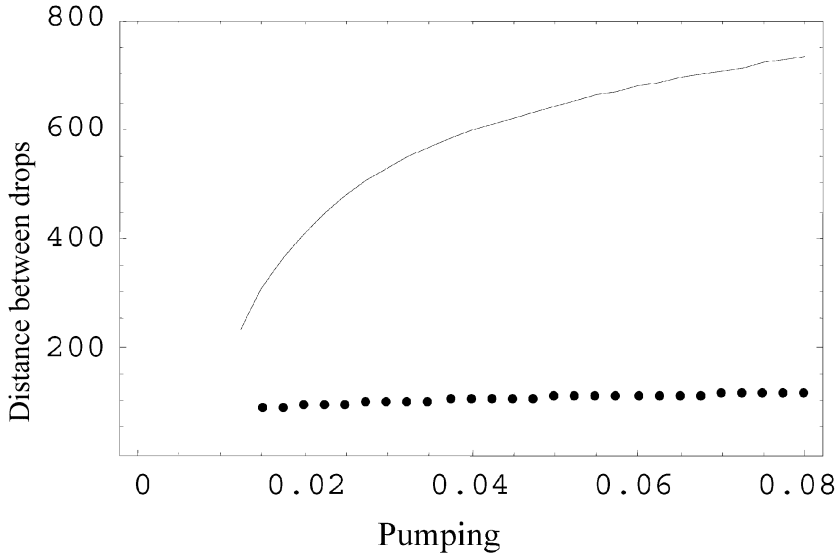

FIGURE 2 The dependence of mean distance between drops (d) on pumping (c_K). The parameters are the same as ones on the Figure 1.

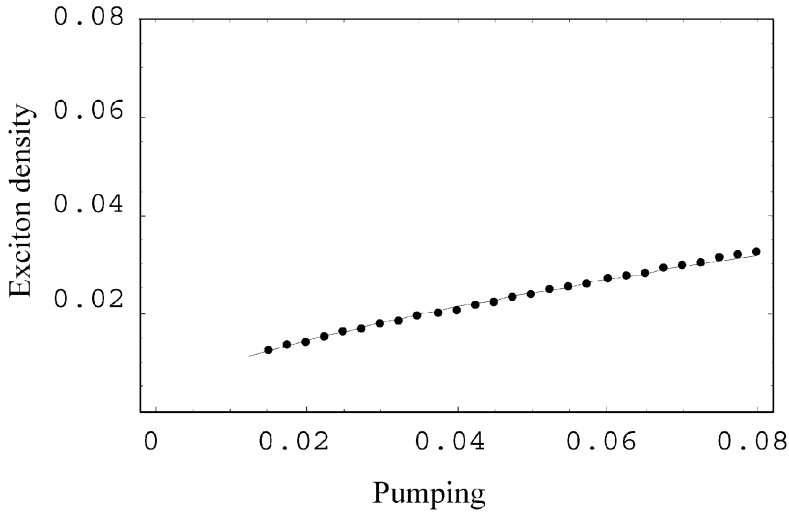

FIGURE 3 The exciton density (c_0) as function of pumping. The parameters are the same as ones on the Figure 1.

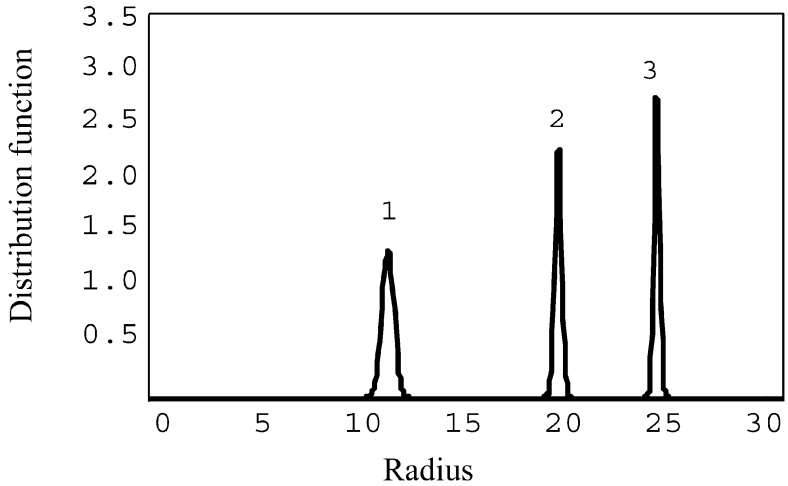

FIGURE 4. The radius distribution function. As function of the radius for different value of pumping. $c_\infty = 0.01, \alpha = 0.1, \nu = 4000, l_D = 100, 1)\ c_K = 0.02, 2)\ c_K = 0.05,$ 3) $c_K = 0.08$.

condensed phase. In organic crystal it has order of $10A^{\circ}$, in semiconductors $20 \div 100A^{\circ}$). The part of excitons, which is occupied in drops, growth with the rise of pumping faster than number of excitons outside of drops. It is important that the both radius of drops and mean distance between them growth with rise of the diffusion coefficient. The exciton density (c_0) (Fig. 3) may differ in several times in comparison with exciton density in absence of drops (i.e. c_K). It is seen from (Fig. 4) the radius distribution function is sharp function of the radius. With decreasing of pumping the function becomes broader.

At large intensities of pumping when the radius becomes compare with distance between drops the mean field approximation used in the article becomes invalid. The correlation between drops should be taking into account.

CONCLUSION

Thus, in the paper the theory is presented which determines the mean radius of drops of exciton condensed phase, the mean distance between drops, the radius distribution function, the drop density distribution function as function of pumping and parameters of crystal such as binding energy of exciton in condensed phase, surface energy, diffusion coefficient, lifetime of exciton, temperature and others.

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