SUPERFLUIDITY IN MOLECULAR CRYSTALS

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In the Frenkel excitonic system [1], as well as in the other quasiparticle system, we can expect collectivization (Bose-Einstein condensation — BEC) and effects of superfluid (SF) transfer (energy, momentum,...) only if the number of such excitations is nearly constant. This condition is satisfied, according to [2], when the time relaxation τ_r of these quasi-particles is smaller than their lifetime τ_l. It is known that the lifetime of optical excitons (according to [1], p. 364) $\tau_l \geqslant 10^{-8}$ s. The time for reaching thermodinamic equilibrium for phonons will be estimated by the standard expression (according to [3]; p. 459):

$$\tau_r = \frac{\hbar}{2\pi} \Big[\sum_{\vec{k},\vec{q}} |M_{if}(\vec{k},\vec{q})|^2 \ \delta (E_i - E_f) \Big]^{-1}, \tag{1}$$

where the energies E and matrix elements of transitions M will be calculated using exciton-phonon interaction Hamiltonian [4]:

$$H_{int} = \sum_{\vec{k},\vec{q}} F(\vec{k},\vec{q})\, B^{+}_{\vec{k}-\vec{q}}\, B_{\vec{k}}\, (b_{-\vec{q}} + b^{+}_{\vec{q}}); \ F(\vec{k},\vec{q}) = i \sqrt{\frac{\hbar \Delta^2}{2MNv_s q}}\ (\vec{q}\, \vec{l}_{\vec{q}}), \tag{2}$$

for the case of scattering of excitons on phonons. Details of these calculations can be found in [5] and we cite only the final result:

$$\tau_r = \frac{3\pi^4 M v_s W}{2\hbar k_B^5 a V \Delta^2} \approx 10^{-13}\ \text{s}. \tag{3}$$

This means $\tau_r << \tau_l$ for Frenkel excitons, and we can expect BEC and all of its consequences in the time interval between 10^{-13} to 10^{-8} s after illumination of crystal.

Analysis of existence of such coupled states in the excitonic system (in the field of mechanical vibrations of crystal lattice) we carried through in papers [6, 7]. Here, we are interested in the consequences of existence of such condensate that is could such BEC — excitonic drop (according to [8]) have a superfluid „motion"? Quasi-particle movement, since they do not have a real mass, has to be conditionally understud in the sence of energy transfer, momentum or some other relevant physical term of the examined system. If „friction" occurs (we use terminology from the standard microtheory SF of liquid He^4 flow, for. ex. [9], p. 133), the drops decay into new excitations. In paper [8] the possibility of bounding excitons into a drop is investigated and the spectar of excitations created in the process of dessintegration of drops is found. Due to the limited space we can only discuss the result:

$$\epsilon(\vec{k}) = \Delta \sqrt{1 - \frac{\sin^2 \Upsilon_0 k}{\Upsilon_0^2 k^2}} . \tag{4}$$

This spectar, linear for small $|\vec{k}| = k$ and quadratic for large k, satisfies the semi-phenomenological condition SF (according to [10], p. 234), that is $\min E(\vec{k})/k > 0$ at the point $\Upsilon_0 k = 4.49$ rad. We have achieved the same conclusion using analysis [11] by the method of Green's functions.

Lately very intensive work is being done on investigation of onedimensional (Id) structures due to its specific orderness as well as the possibility of treating the anisotropy as the break in symmetry along one direction only. Therefore we decided to look for the spectar of elementary excitations in molecilar chains where BEC of excitons exists [12]. Therefore, we investigate 1-d excitonic system coupled with (the only possible!) longitudinal phononic branch:

$$H = H_{ex} + H_{ph} + H_{ex-ph}, \tag{5}$$

where

$$H_{ex} = \sum_{\vec{k}} \epsilon_{ex}(k) B_{\vec{k}}^{+} B_{\vec{k}}; \qquad \epsilon_{ex}(k) = \Delta - 2 W \cos a k,$$

$$H_{ph} = \sum_{\vec{k}} \epsilon_{ph}(k) b_{\vec{k}}^{+} b_{\vec{k}}; \qquad \epsilon_{ph}(k) = \hbar v_s k, . \tag{6}$$

are the standard Hamiltonians of excitonic and phonon subsystems, and H_{ex-ph} describes their interaction given by (2).

Using the procedure similar to the one used in BCS theory of superconductivity (Frölich and Bogolyubov's u-v transformation, ...) we arrive to the dispersion law of elementary excitations (see in [12]).

$$E(k) = \sqrt{\epsilon^2_{ex}(k) - |\phi(k)|^2} \tag{7}$$

Here ϕ (k) are the transformation functions defining the gap elementary excitations and satisfying the gap- equation:

$$\phi(k) + \frac{1}{N}\sum_q \frac{T(k,q)}{E(q)}\phi(q) = 0; \qquad T(k,q) = -\frac{2m^2\Delta^2}{M\hbar^2}[k_o{}^2 - (k-q)^2], \tag{8}$$

and represents the singular kernel of this equation. This very complicated singular difference equation can be solved using a new method (presented on the VIII th Congr. of Phys. Math. Astr. of Yugoslavia in Priština, 1985) given in the paper [12]. The results of such procedure, after the numerical calculations are represented graphically (Figs 1 and 2).

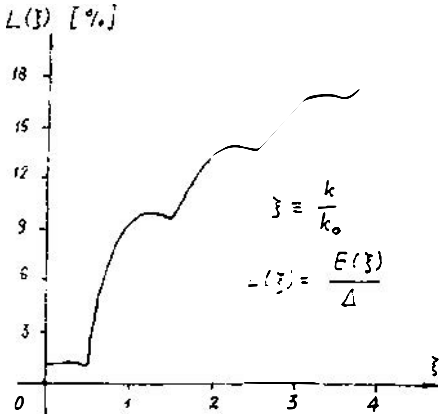

Fig. 1

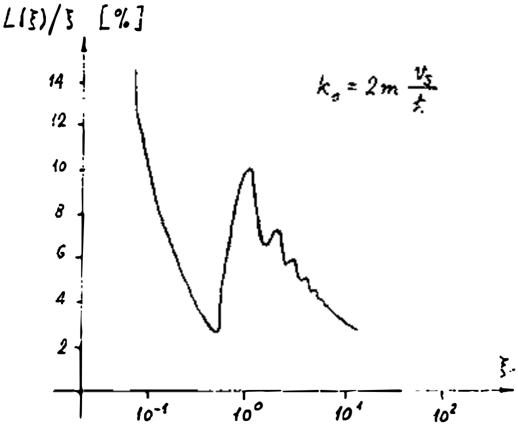

Fig. 2

We see from figures that function E(k)/k (phase velocity) has several positive minima, located in the vicinity of the points nk_o (n = 1, 2, . . .) and that it satisfies Landau criterion of SF in the entire momentum region of the first Brillouin zone. This brings to a conclussion that we can expect in ld excitonic system SF effects.

If there exists in the molecular chains exciton-phonon interaction, such that quasi-particles with velocity (v) smaller than the longitudinal sound velocity (v_s) are created, they will behave as the solitary waves [13]. The probability amplitudes A (n, t) of single particle solitary states ($|\phi\rangle = \sum_n A(n,t)\, B_n^+ |oc\rangle$) satisfies the following „solitary" equation (the formation of such, cubic Schrödinger equation can be found in [14]):

$$i\hbar\frac{\partial A}{\partial t} - (\hbar\Omega + E_p)A + a^2 W\frac{\partial^2 A}{\partial x^2} + \frac{4a^2 (J_\Delta - J_W)^2}{M(v_s{}^2 - v^2)}|A|^2 A = 0. \tag{9}$$

When the quasi-particles are created in the system with the velocities $v > v_s$, this equation, however, changes its meaning, since the last term becomes negative. In this case, it gets the form like the phenomenological equation of hydrodynamics that describes SF liquid flow [15]. This equation is then satisfied by the plane wave whose the elementary excitations („shifted excitons") energy is:

$$\epsilon (k) = \Delta - 2W + Wa^2k^2 + E_p + \frac{\hbar^2 (J_\Delta - J_W)^2}{MNa^2 W^2} (k^2 - k_s^2)^{-1}. \qquad (10)$$

This dispersion law satisfies allready mentioned superfluidity criterion, min $\epsilon (\eta)/\eta > 0$ ($\eta = k/k_s$) at point $\eta_m = 62$.

It has to be mentioned at the end, that investigating the possibility of excitonic SF using the scattering mechanism of exciton on exciton which here, due to the limited spance, can only be cited. In the case of higher excitonic concentrations ($\sim 10^{-3}$ when exciton-exciton interaction is predominant [16]), the spectrum of excitation energy is found and shown that it satisfies micro-theoretical criterion [17] and equation of motion is formed under the conditions of existence of coherent excitonic states [5]. These results confirm that we can expect SF transfer of excitons in molecular crystals although the phonons are not present. We can conclude on the basis of what was said above without doubt that molecular crystals satisfy all of the micro-and macro-theoretical SF criteria and that we can expect SF transfer of optical excitations, that is, that molecular crystals possess SF characteristics. There still remains open the question of „drift", that is the problem of the methods of directing of these excitations so that the effect could be in practice and gainfully used.

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