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ON SOME POSSIBLE CONSEQUENCES OF EXCITON-PHONON INTERACTION IN MOLECULAR CRYSTALS WITH TWO SUBLATTICES

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ABSTRACT. Applying the Frölich transformation to the Hamiltonian of the system excitons+phonons in molecular crystals with comples lattice, we have shown that exciton-phonon interaction can lead to the fusion of two excitons into exciton drops. We hawe examined the spectrum of elementary excitations formed through the decay of the drop and we have demonstrated that it satisfies the superfluidity condition.

We shall discuss exciton-phonon interaction in molecular crystals with two molecules in an ellementary cell, in the approximation of strong exciton-phonon coupling[1]. As it was demonstrated, interaction with the longitudinal phonon branch is dominant, so we shall keep only that part of interaction in the Hamiltonians

$$H = H_{ex} + H_f + H_{int} \tag{1}$$

The exciton Hamiltonian in harmonic approximation has the following form

$$H_{ex} = \sum_{\mu,\vec{k}} E_\mu(\vec{k}) B^+_\mu(\vec{k}) B_\mu(\vec{k}) \quad , \quad \mu = 1,2 \tag{2}$$

where B^+_μ creates exciton in μ -band with the energy $E_\mu(\vec{k})$. In the case of two sublattices exciton energy bands are given as[2]

$$E_{1/2}(\vec{k}) = \frac{\Delta_1+\Delta_2+L_{11}(\vec{k})+L_{22}(\vec{k})}{2} \pm \sqrt{\left(\frac{\Delta_1-\Delta_2+L_{11}(\vec{k})-L_{22}(\vec{k})}{2}\right)^2 + L_{12}(\vec{k})L_{21}(\vec{k})} \tag{3}$$

where $\Delta_{1,2}$ is the excitation energy of an isolated molecule and $L_{\alpha\beta}(\vec{k})$ are the dipole-dipole interaction matrix elemments.

The Hamiltonian describing the longitudinal phonon branch is

$$H_f = \sum_{\vec{q}} E_f(\vec{q}) a^+_{\vec{q}} a_{\vec{q}} \quad ; \quad E_f(\vec{q}) = \hbar v |\vec{q}| \tag{4}$$

with standard meaning of terms.

The exciton-phonon interaction is given by[1]

$$H_{int} = \sum_{\mu\mu'\vec{K}\vec{q}} \Phi_{\mu\mu'}(\vec{K}\vec{q}) B^+_{\mu}(\vec{K}-\vec{q}) B_{\mu'}(\vec{K}) \left(a_{-\vec{q}} + a^+_{\vec{q}} \right) \tag{5}$$

where

$$\Phi_{\mu\mu'}(\vec{K}\vec{q}) = \frac{i}{\sqrt{N}} \sum_{\alpha=1}^{2} \overset{*}{U}_{\alpha\mu}(\vec{K}-\vec{q}) U_{\alpha\mu'}(\vec{K}) \Delta_\alpha \left(\frac{\hbar q}{2M_\alpha v} \right)^{1/2} \tag{6}$$

N -is the number of ellementary cells and M_α is the molecular mass. The matrix $U = \| U_{\alpha\beta}(\vec{K}) \|$ diagonalizes the exciton Hamiltonian (2). The explicite form of this matrix is given in[2].

Performing the Frolich[3] transformation

$$H' = e^{-S} H e^{S} \approx H - [S,H] + \frac{1}{2} [S,[S,H]] \tag{7}$$

where

$$S = \sum_{\mu\nu\vec{K}\vec{q}} \frac{\Phi_{\mu\nu}(\vec{K}\vec{q})}{E_\nu(\vec{K}) - E_\mu(\vec{K}-\vec{q}) + E_f(\vec{q})} B^+_{\mu}(\vec{K}-\vec{q}) B_\nu(\vec{q}) a_{-\vec{q}} - C.C. \tag{8}$$

and averaging over the phonon ground state, we obtain an effective exciton-exciton interaction. It can become attractive in a certain region of wave vectors[4],[5], and cause the formation of exciton drops[6].

The part of the hamiltonian responsible for such a process is

$$H_c = \sum_{\mu\vec{K}} E_\mu(\vec{K}) B^+_\mu(\vec{K}) B_\mu(\vec{K}) + \sum_{\mu\nu\vec{K}\vec{q}} J_{\mu\nu}(\vec{K}\vec{q}) B^+_\mu(\vec{K}) B^+_\mu(-\vec{K}) B_\nu(-\vec{q}) B_\nu(\vec{q}) \tag{9}$$

with

$$J_{\mu\nu}(\vec{K}\vec{q}) = \frac{E_f(\vec{K}+\vec{q}) \overset{*}{\Phi}_{\nu\mu}(\vec{K}, \vec{K}+\vec{q}) \Phi_{\mu\nu}(\vec{q}, \vec{K}+\vec{q})}{\left[E_\mu(\vec{K}) - E_\nu(\vec{q}) \right]^2 - E_f^2(\vec{K}+\vec{q})} \tag{10}$$

Following the ideas of Bogolyubov[7)], we diagonalize the Hamiltonian (9) by canonical transformation

$$B_\mu(\vec{k}) = U_\mu(\vec{k})C_\mu(\vec{k}) + V_\mu(\vec{k})C_\mu(-\vec{k}) \;;\; U_\mu^2(\vec{k}) - V_\mu^2(\vec{k}) = 1 \tag{11}$$

Substituting (11) into (9) we obtain the quadratic part of the Hamiltonian in the form

$$H_c^{(2)} = \sum_{\mu\vec{k}} \sqrt{E_\mu^2(\vec{k}) - \Psi_\mu^2(\vec{k})}\,\left(C_\mu^+(\vec{k})C_\mu(\vec{k}) + C_\mu^+(-\vec{k})C_\mu(-\vec{k})\right) \tag{12}$$

The functions $\Psi_\mu(\vec{k})$ are defined by the following system of integral equations

$$\Psi_\mu(\vec{k}) + \sum_{\nu\vec{q}} \frac{J_{\mu\nu}(\vec{k},\vec{q})}{\sqrt{E_\nu^2(\vec{q}) - \Psi_\nu^2(\vec{q})}}\,\Psi_\nu(\vec{q}) = 0 \tag{13}$$

We shall solve it under the assumptions

1° $L_{12}(\vec{k}) \gg \Delta_1 - \Delta_2 + L_{11}(\vec{k}) - L_{22}(\vec{k})$; 2° $L_{12}(\vec{k}) \ll \Delta_1 - \Delta_2 + L_{11}(\vec{k}) - L_{22}(\vec{k})$

in which case[2)] the matrix elements are wave vector independent, i. e. $U_{\alpha\beta}(\vec{k}) = U_{\alpha\beta}(0)$. If $E_\mu(\vec{k}) \approx E_\mu(0) \gg \Psi_\nu(\vec{k})$, instead of (13), the following approximate system of singular integral equations is obtained

$$\Psi_\mu(\vec{k}) + \frac{2m^{*2}V}{(2\pi)^3\hbar^2}\sum_{\nu=1}^{2}\frac{G_{\mu\nu}}{E_\nu(0)}\int d^3\vec{q}\,\frac{\Psi_\nu(\vec{q})}{(\vec{k}-\vec{q})^2 - (K_0^2 + Q_{\mu\nu}^2 - P_{\mu\nu}^2)} = 0 \tag{14}$$

with

$$G_{\mu\nu} = \sum_{\alpha\alpha'=1}^{2}\frac{\Delta_\alpha}{M_\alpha}\frac{\Delta_{\alpha'}}{M_{\alpha'}}U_{\alpha\mu}^*(0)U_{\alpha\nu}(0)U_{\alpha'\nu}(0)U_{\alpha'\mu}^*(0) \quad ,$$

$$K_0 = \frac{2m^*V}{\hbar} \quad , \quad Q_{\mu\nu}^2 = -\frac{4m^*\Delta_{\mu\nu}}{N^2\hbar^2}\sum_{\vec{k}\vec{q}}\frac{k^2-q^2}{(\vec{k}+\vec{q})^2} \approx \frac{4m^*\Delta_{\mu\nu}}{35\,\hbar^2}$$

$$P_{\mu\nu}^2 = \left(\frac{2m^*\Delta_{\mu\nu}}{\hbar^2}\right)^2\frac{1}{N^2}\sum_{\vec{k}\vec{q}}\frac{1}{(\vec{k}+\vec{q})^2} \approx \frac{21}{10}\left[\frac{2\Delta_{\mu\nu}m^*}{\hbar^2\mu_c^2}\right]^2\mu_0^2$$

where: m^* is the effective exciton mass, $\Delta_{\mu\nu} \equiv E_\mu(0) - E_\nu(0)$ and

$\mu_0 = \frac{1}{a}(6\pi^2)^{1/2}$ the boundari vector of the first Brillouin zone.

After a Fourier transformation of (14)[4] we find two general solutions

$$\Psi_1(\vec{k}) = C\,\frac{\sin Rk}{Rk}\,, \qquad \Psi_2(\vec{k}) = -C\lambda\,\frac{\sin Rk}{Rk} \tag{15}$$

where C is an arbitrary constant, $R = \frac{\pi}{2K_0} \approx 10^{-5}\,\mathrm{cm}$,

$$\lambda = \frac{E_2(0)\,\hbar^2}{2w^{*2} V G_{11} Y_{12}(R)}\left[1 + \frac{2w^{*2} V G_{11}}{E_1(0)\,\hbar^2}\right] \quad \text{and}$$

$$Y_{\mu\nu}(\vec{r}) = \frac{1}{(2\pi)^3}\int d^3\vec{\lambda}\,\frac{e^{-i\vec{r}\vec{\lambda}}}{\lambda^2 - (K_0^2 + Q_{\mu\nu}^2 - P_{\mu\nu}^2)}$$

If we determine C so that $\mathcal{E}_1(\vec{k}) \equiv \sqrt{E_1^2(0) - \Psi_1^2(\vec{k})} \to 0$ for $\vec{k} \to 0$ we finally find the energies of elementary excitations

$$\mathcal{E}_1(\vec{k}) = E_1(0)\sqrt{1 - \frac{\sin^2 Rk}{R^2k^2}} \tag{16}$$

$$\mathcal{E}_2(\vec{k}) = \sqrt{E_2^2(0) - E_1^2(0)\,\lambda^2\,\frac{\sin^2 Rk}{R^2k^2}} \tag{17}$$

Analysing (16) we find for the small $\vec{k}$

$$\mathcal{E}_1(\vec{k}) \approx C_0\,\hbar k \quad ; \quad C_0 = \sqrt{\frac{2}{3}}\,\frac{E_1(0)R}{\hbar} \approx 10^9\,\mathrm{cm\,s^{-1}} \tag{18}$$

which corresponds to the dispersion law of the light quanta.

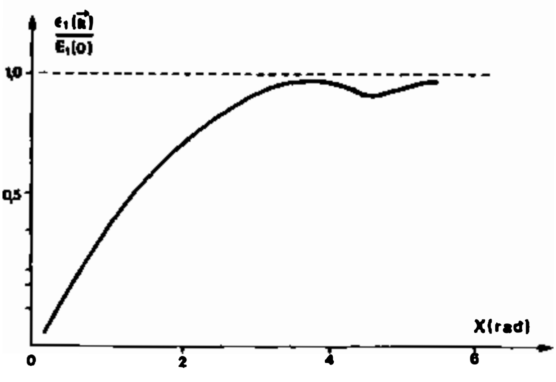

Fig. 1

The spectrum (16) is given on Fig. 1. The characteristic minimum, analogous to the rotonic one in the theory of liquid He^4, shows that the excitations can move like a superfluid trough the crystal.

The other branch $\mathcal{E}_2(\vec{k})$ is damped for $K \leq 10^6 cm^{-1}$ and becomes quasilinear for $K > 10^6 cm^{-1}$

In the case of two identical molecules, these two branches coincide

$$\mathcal{E}_{1,2}(\vec{k}) = E_{1,2}(0)\sqrt{1-\frac{\mathcal{J}in^2 R_K}{R^2K^2}} \tag{19}$$

and they both satisfy Landau's superfluidity condicion.

Spectrum (16), characteristics of the curve are: coordinates of the minimum M(4,5 ; o,97) ; the rotonic deviation $\left(E_1(0)-\mathcal{E}_1\right)_{x=4,5}$ is $4\% \, E(0) \approx 10^{-1} eV$.

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