

Electron-hole fluid in polar semiconductors

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We evaluate the binding energy of an electron-hole fluid taking into account the interaction of the electrons and holes with longitudinal optical phonons. We show that the contribution from that interaction increases the stability of the liquid phase with respect to a decay into free excitons or exciton molecules.

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For the theoretical study of the electron-hole fluid—the condensed phase of non-equilibrium carriers in semiconductors^[1]—one usually employs^[2-6] the Hamiltonian

$$H = \sum_{\mathbf{p}s} [E_e(\mathbf{p}) a_{e\mathbf{p}s}^+ a_{e\mathbf{p}s} + E_h(\mathbf{p}) a_{h\mathbf{p}s}^+ a_{h\mathbf{p}s}] + \frac{1}{2} \sum_{\mathbf{p}\mathbf{p}'\mathbf{k}\mathbf{s}\mathbf{s}'} V(\mathbf{k}) (a_{e\mathbf{p}\mathbf{k}\mathbf{s}}^+ a_{e\mathbf{p}'\mathbf{k}\mathbf{s}'} a_{e\mathbf{p}'\mathbf{k}\mathbf{s}} a_{e\mathbf{p}\mathbf{k}\mathbf{s}} + a_{h\mathbf{p}\mathbf{k}\mathbf{s}}^+ a_{h\mathbf{p}'\mathbf{k}\mathbf{s}'} a_{h\mathbf{p}'\mathbf{k}\mathbf{s}} a_{h\mathbf{p}\mathbf{k}\mathbf{s}} - 2a_{e\mathbf{p}\mathbf{k}\mathbf{s}}^+ a_{h\mathbf{p}'\mathbf{k}\mathbf{s}'} a_{h\mathbf{p}'\mathbf{k}\mathbf{s}} a_{e\mathbf{p}\mathbf{k}\mathbf{s}}), \quad (1)$$

where the indices *e* and *h* indicate quantities referring, respectively, to electrons and holes, $E_{e(h)}(\mathbf{p})$ is the energy as function of the quasi-momentum, $a_{e(h)\mathbf{p}s}^+$ and $a_{e(h)\mathbf{p}s}$ are fermion creation and annihilation operators for particles in a state with quasi-momentum \mathbf{p} and spin *z*-component *s*,

$$V(\mathbf{k}) = 4\pi e^2 / \epsilon k^2 \quad (2)$$

is the Fourier transform of the Coulomb interaction, and ϵ is the dielectric constant of the crystal which, as a rule, is assumed to be constant,

However, in the case of crystals with a partially ionic binding it may turn out that the assumption that ϵ is constant is unjustified. Taking into account the longitudinal oscillations of the crystalline lattice leads, as is well known,^[7] to a strong dispersion of ϵ in the region of low frequencies ω :

$$\epsilon(\omega) = \epsilon_\infty \epsilon_0 \frac{\omega_l^2 - \omega^2}{\epsilon_\infty \omega_l^2 - \epsilon_0 \omega^2}, \quad (3)$$

where ω_l is the frequency of a longitudinal optical phonon, ϵ_0 and ϵ_∞ are the static ($\omega \rightarrow 0$) and high-frequency ($\omega \gg \omega_l$) values of ϵ .

In order to take the dispersion $\epsilon(\omega)$ into account we add to the Hamiltonian (1) a term describing the interaction of the electrons and holes with the optical phonons:

$$H = \sum_{\mathbf{p}\mathbf{k}} g(\mathbf{k}) (c_{\mathbf{k}} + c_{-\mathbf{k}}^+) (a_{e\mathbf{p}+\mathbf{k}}^+ a_{e\mathbf{p}} + a_{h\mathbf{p}+\mathbf{k}}^+ a_{h\mathbf{p}}), \quad (4)$$

where

$$g(\mathbf{k}) = \left(\frac{2\pi e^2}{k^2} \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0} \hbar \omega_l \right)^{1/2}, \quad (5)$$

$c_{\mathbf{k}}^+$ and $c_{\mathbf{k}}$ are creation and annihilation operators for an optical phonon with quasimomentum \mathbf{k} and we put in (2) $\epsilon = \epsilon_\infty$. In what follows we shall use a system of units where $m = e = \hbar = 1$, where *m* is the reduced mass of the electron or hole.

In the random-phase approximation we get for the interaction energy (the sum of the exchange and correlation energies) the well-known formula (see, e.g.,^[8])

$$E_{int}^e = -\frac{3\pi^2}{p_F^3} \text{Re} \int \frac{dk}{(2\pi)^3} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi i} \int_0^1 \frac{d\lambda}{\lambda} \frac{\lambda V(\mathbf{k}) \Pi_e(\mathbf{k}, \omega)}{1 - \lambda V(\mathbf{k}) \Pi_e(\mathbf{k}, \omega)}. \quad (6)$$

Here $p_F = (3\pi^2 n)^{1/3}$ is the Fermi momentum and *n* the electron (hole) density,

$$\Pi_e(\mathbf{k}, \omega) = 2 \int \frac{d\mathbf{p}}{(2\pi)^3} \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi i} G_0^e(\mathbf{p}, \epsilon) G_0^e(\mathbf{p}+\mathbf{k}, \epsilon+\omega) \quad (7)$$

is the electron polarization operator, $G_0^e(\mathbf{p}, \epsilon)$ the electron Green function:

$$G_0^e(\mathbf{p}, \epsilon) = \frac{1}{\epsilon - E_e(\mathbf{p}) + i\delta \text{sign}(p - p_F)}, \quad \text{sign } x = \begin{cases} 1, & x > 0, \\ -1, & x < 0, \end{cases} \quad \delta \rightarrow +0. \quad (8)$$

To generalize Eq. (6) to the case of electrons and holes interacting with optical phonons we introduce in (6) instead of $\Pi_e(\mathbf{k}, \omega)$ the polarization operator

$$\Pi(\mathbf{k}, \omega) = \Pi_0(\mathbf{k}, \omega) + \Pi_i(\mathbf{k}, \omega), \quad \Pi_0(\mathbf{k}, \omega) = \Pi_e(\mathbf{k}, \omega) + \Pi_h(\mathbf{k}, \omega), \quad (9)$$

where $\Pi_i(\mathbf{k}, \omega)$ is the ion polarization operator

$$V(\mathbf{k}) \Pi_i(\mathbf{k}, \omega) = \gamma(\omega) = \frac{\omega_l^2 - \omega^2}{\omega^2 - \omega_l^2 + i\delta}, \quad (10)$$

and we subtract from the expression obtained for E_{int} the purely ion contribution. As a result we get

$$E_{int}^e = -\frac{3\pi^2}{p_F^3} \text{Re} \int \frac{dk}{(2\pi)^3} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi i} \int_0^1 \frac{d\lambda}{\lambda} \left[\frac{\lambda V(\mathbf{k}) \Pi(\mathbf{k}, \omega)}{1 - \lambda V(\mathbf{k}) \Pi(\mathbf{k}, \omega)} - \frac{\lambda V(\mathbf{k}) \Pi_i(\mathbf{k}, \omega)}{1 - \lambda V(\mathbf{k}) \Pi_i(\mathbf{k}, \omega)} \right]. \quad (11)$$

Replacing here the integration over λ by an integration over

$$\tilde{\lambda} = \frac{1 - \gamma(\omega)}{1 - \gamma(\omega)\lambda},$$

we get

$$E_{int}^e = -\frac{3\pi^2}{p_F^3} \text{Re} \int \frac{dk}{(2\pi)^3} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi i} \int_0^1 \frac{d\tilde{\lambda}}{\tilde{\lambda}} \frac{\tilde{\lambda} V(\mathbf{k}, \omega) \Pi_0(\mathbf{k}, \omega)}{1 - \tilde{\lambda} V(\mathbf{k}, \omega) \Pi_0(\mathbf{k}, \omega)}, \quad (12)$$

where

$$\Gamma(\mathbf{k}, \omega) = V(\mathbf{k}) \epsilon_\infty / \epsilon(\omega) = V(\mathbf{k}) + g^2(\mathbf{k}) D_0(\mathbf{k}, \omega). \quad (13)$$

$$D_0(\mathbf{k}, \omega) = 2\omega_l^2 / (\omega^2 - \omega_l^2 + i\delta). \quad (14)$$

The expression (12) for the interaction energy of the electron-hole system, taking the optical phonons into account, reduces thus to the analogous expression (6) for the electron gas with $V(\mathbf{k})$ replaced by $\tilde{V}(\mathbf{k}, \omega)$ or, to adding to $V(\mathbf{k})$ the optical phonon Green function (with the appropriate factor $g^2(\mathbf{k})$).

We note that one can also perform a similar transformation in the Hubbard approximation^[8] but in the more general case when $\Pi(\mathbf{k}, \omega)$ is not evaluated in lowest order, an equation such as (12) does not occur, i.e., taking the interaction with the phonons into account does in the general case not reduce to replacing $V(\mathbf{k})$ by $\tilde{V}(\mathbf{k}, \omega)$.

We restrict ourselves in what follows to the case of isotropic and non-degenerate electrons and hole bands with effective masses m_e and m_h ; in that case

$$E_e(\mathbf{p}) = \frac{p^2}{2(1+\sigma)m}, \quad E_h(\mathbf{p}) = \frac{p^2}{2(1+1/\sigma)m},$$

$$\frac{1}{m} = \frac{1}{m_e} + \frac{1}{m_h}, \quad \sigma = \frac{m_e}{m_h}, \quad (15)$$

and one sees easily that the quantities characterizing holes can be obtained from the corresponding quantities characterizing electrons by changing σ to $1/\sigma$.

The electron exchange energy has the form

$$E_{ex}^e = -\frac{6\pi^2}{p_F} \int \frac{dp dq i d\epsilon i d\omega}{(2\pi)^8} G_0^e(\mathbf{p}, \epsilon) G_0^e(\mathbf{q}, \omega) V(\mathbf{p}-\mathbf{q}, \epsilon-\omega), \quad (16)$$

and its evaluation reduces to a single integral

$$E_{ex} = -\frac{3}{\pi} \frac{p_F}{\epsilon_\infty} \left\{ 1 + \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0} (I_e + I_h) \right\}, \quad (17)$$

$$I_e = \frac{1}{\beta_e} \left\{ \frac{\pi^2}{8} + \frac{1}{2\beta_e} \int_0^1 \frac{dx x}{(1-x^2)^2} \ln \frac{1+\beta_e(1-x^2)}{1+\beta_e(1/x^2-1)} \ln \frac{1+x}{1-x} \right\}, \quad (18)$$

$$\beta_e = E_F^e/\omega_i, \quad E_F^e = p_F^2/2(1+\sigma), \quad (19)$$

which can be simply evaluated in two limiting cases: $\beta_e \ll 1$ and $\beta_e \gg 1$.

We consider the case $\beta_{e,h} \ll 1$. In this case

$$E_{ex} = E_p + E_{ex}^0(1 + \Delta_{ex}); \quad (20)$$

the first term is here the polaron shift (renormalization of the width of the forbidden band^[7]):

$$E_p = -\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \left(\frac{\omega_i}{2} \right)^{1/2} \left[(1+\sigma)^{1/2} + \left(1 + \frac{1}{\sigma} \right)^{1/2} \right] \quad (21)$$

and will be dropped in what follows, E_{ex}^0 is the exchange energy where taking the interaction with the optical phonons into account reduces to replacing ϵ_∞ by ϵ_0 :

$$E_{ex}^0 = -\frac{3}{2\pi} \frac{p_F}{\epsilon_0} = -\frac{3}{2^{1/2}\pi\epsilon_0} \left[(\beta_e\omega_i(1+\sigma))^{1/2} + \left(\beta_h\omega_i \left(1 + \frac{1}{\sigma} \right) \right)^{1/2} \right] \quad (22)$$

$$\Delta_{ex} = \frac{\epsilon_0 - \epsilon_\infty}{3\epsilon_\infty} \left[1 + \frac{\pi}{10} (\beta_e^{1/2} + \beta_h^{1/2}) + \dots \right]; \quad (23)$$

in view of the fact that $\Delta_{ex} > 0$ the exchange energy increases (in absolute magnitude) relative to E_{ex}^0 , but decreases relative to the exchange energy (25) evaluated without taking the interaction with the optical phonons into account at all ($\epsilon = \epsilon_\infty$).

In the opposite limiting case, $\beta_{e,h} \gg 1$, we get (subtracting the polaron shift)

$$E_{ex} = E_{ex}^0(1 + \Delta_{ex}) - E_p, \quad (24)$$

where

$$E_{ex}^0 = -\frac{3}{2\pi} \frac{p_F}{\epsilon_\infty} = -\frac{3}{2^{1/2}\pi\epsilon_\infty} \left[(\beta_e\omega_i(1+\sigma))^{1/2} + \left(\beta_h\omega_i \left(1 + \frac{1}{\sigma} \right) \right)^{1/2} \right] \quad (25)$$

is the exchange energy when the interaction with the optical phonons is neglected,

$$\Delta_{ex} = \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0} \frac{\pi^2}{8} \left\{ \frac{1}{\beta_e} + \frac{1}{\beta_h} - \frac{1}{\pi^2} \left(\frac{1}{\beta_e^2} \ln^2 \beta_e + \frac{1}{\beta_h^2} \ln^2 \beta_h \right) + \dots \right\}; \quad (26)$$

in this limiting case the exchange energy is thus also in absolute magnitude less (due to the term E_p) than when the optical phonons are neglected.

To evaluate the correlation energy we used the Nozieres-Pines method^[9] (for details see^[2]) which reduces to the random phase approximation for small momentum transfer ($k \ll p_F$), for large momentum transfer ($k \gg p_F$) to second order perturbation theory, and interpolations between them. Numerical estimates showed that in both cases, $\beta_{e,h} \ll 1$ and $\beta_{e,h} \gg 1$, the main contribution comes from a correction to the exchange energy (the corrections to the correlation energy are an order of magnitude smaller) and in what follows

we omit the corrections to the correlation energy. Moreover, we shall in the following consider only the case $\beta_{e,h} \ll 1$.

From the expression (20) to (26) obtained above it follows that although the interaction with the optical phonons decreases the binding energy of the electron-hole fluid, in view of the fact that decrease in the exciton binding energy E_B is larger, $\propto \epsilon_\infty^2/\epsilon_0^2$ ^[10]

$$E_B = E_x \left\{ 1 + \frac{2E_x}{(2\omega_i)^{1/2}} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \left[\frac{3}{8} \frac{(1+\sigma)^{1/2}(1+\sigma^{1/2})}{\sigma^2} - \frac{1}{3} \frac{(1+\sigma)^{1/2}(1+\sigma^{1/2})}{\sigma} \right] \right\}. \quad (27)$$

The binding energy of the electron-hole fluid increases relative to the free exciton gas. Taking the interaction with the optical phonons into account through replacing ϵ_∞ by ϵ_0 gives a lowered value for the binding energy of the electron-hole plasma.

When making numerical estimates we change to the system of units usually employed in similar problems^[2-6] in which the energy is measured in effective Rydbergs, $E_X = me^4/2\epsilon_0^2\hbar^2$, distances in effective Bohr radii, $a_X = \epsilon_0\hbar^2/me^2$, and introduce the dimensionless parameter $r_S = (3/4\pi n a_X^3)^{1/3}$. Moreover, since the correlation energy is lowered in our method (e.g., for the electron-hole pair energy $E_0(r_S, \sigma)$ our method gives for $\sigma = 1$, $r_S = 2$: $E_0 = -0.75$, and the method used in^[3] gives $E_0 = -0.86$ and in^[4] $E_0 = -0.99$), we give only the amount of the increase in the pair energy ΔE when the interaction of the electrons and holes with the optical phonons is taken into account more exactly. To obtain the total pair energy \tilde{E} we must add to ΔE the quantity E_0 obtained by more exact methods. In view of the fact that the main contribution to ΔE comes from the corrections to the exchange energy which were evaluated exactly, and as $|\Delta E| \ll E_0$ errors arising from such a substitution are insignificant.

If we restrict ourselves to the first terms in (23) we find for the case $\beta_{e,h} \ll 1$ that when

$$(\epsilon_0 - \epsilon_\infty)/\epsilon_0 \geq \pi(4/9\pi)^{1/2} r_S [1 + E_0(r_S, \sigma) + E_D(\sigma)], \quad (28)$$

where $E_D(\sigma)$ is the dissociation energy of a bi-exciton (the change in the binding energy of the exciton (bi-exciton) can be neglected when $\beta_{e,h} \ll 1$), the electron-hole plasma will in semi-conductors with isotropic non-degenerate bands be energetically more advantageous than the bi-exciton gas. For instance, if we take $E_0(r_S = 2, \sigma = 1) = -0.99$,^[4] $E_D(\sigma) = 0.029$,^[11] we get $(\epsilon_0 - \epsilon_\infty)/\sigma_0 \geq 0.13$.

For gallium arsenide (case $\beta_{e,h} \ll 1$), taking $\hbar\omega_i = 36.22$ meV, $\epsilon_0 = 12.9$, $\epsilon_\infty = 10.9$,^[10] and $\sigma = 0.105$ ^[9] we get $\Delta E = -0.23$ meV for an equilibrium density $n = 1.59 \times 10^{16}$ cm⁻³, corresponding to $E_0 = -4.08$ meV.^[9] Thus, $\tilde{E} = -4.31$ meV while the experimental value of the binding energy of an exciton equals 4.2 ± 0.2 meV.^[12] We note that for gallium arsenide the experimental value of the binding energy of 4.2 ± 0.2 meV is larger than $E_X = 3.7$ meV which is connected with taking into account the degeneracy of the hole bands. A more exact calculation^[13] gives an exciton binding energy of 4.15 meV. The inclusion of the interaction with the optical phonons changes the calculated value of the exciton binding energy in gallium arsenide only by 0.1%.^[10]

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