Thermodynamics of electron–hole fluctuations and formation of exciton phase in layered semiconductor structures

E. A. Zhukovskiĭ and V. V. Tugushev
Kurchatov Institute Russian Science Center, 123182 Moscow, Russia

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The thermodynamics of the formation of an exciton phase in a layered semiconductor structure with a narrow band gap is analyzed in a model in which the phase of the order parameter is strictly fixed. Calculations are carried out in a self-consistent fluctuation theory for static fluctuations of the amplitude of the order parameter. The temperature of the transition to the exciton phase derived for the case with fluctuation effects (T_c) is much lower than the temperature calculated in the mean-field approximation (T_c^0). The phase transition at T_c is of first order. In a quasi-2D system, the temperature of the supercooling of the normal phase, T' $(T'<T_c)$, is nonzero, while in a purely 2D situation we would have $T'=0$. The temperature of the superheating of the exciton phase is $T''>T_c$. A phase with a short-range order exists over the broad temperature range $T_c<T<T_c^0$.

1. The thermodynamics of systems with electron–hole pairing has been worked out well for the model of an "exciton insulator" with a semimetallic spectrum of quasiparticles. Since there is a small parameter here, $T_c/\epsilon_F \sim \exp(-1/U) \ll 1$ for $U \ll 1$ (T_c is the transition temperature, ϵ_F is the Fermi energy, and U is the interaction constant), we can make effective use of the mean-field approximation in this model, as in the BCS model in the theory of superconductivity.[1]

In the case of a semiconducting spectrum,[2] we are confronted by the entire question of constructing a thermodynamics of electron–hole fluctuations and of their effect on the temperature and nature of the transition to the exciton phase. It is easy to show that the mean-field approximation yields only a purely symbolic estimate of T_c: $T_c^0 \sim E_g/|\ln\Theta|$, where $\Theta=(E_{ex}/E_g-1)\sim(U/U_0-1)$, E_g is the width of the band gap, and E_{ex} is the binding energy in the exciton. The condition for an exciton instability ($\theta>0$) holds only if the interaction constant is sufficiently large: $U>U_0$, where U_0 is the interaction for which we have $E_g=E_{ex}$. The situation here stands in contrast with the semimetallic model, in which the instability occurs at arbitrarily small values of U. It would seem that the thermodynamics of the semiconductor model should be similar to that of the Stoner model, in which a governing role is played by fluctuations of the order parameter, not by the temperature dependence of the mean-field characteristics. Below we discuss a "self-consistent fluctuation theory," in which the role of the small parameter is played directly by the quantity $\theta \ll 1$ (by analogy with the approach of Ref. 3). This theory predicts a transition temperature T_c which is sharply lower than that of the mean-field approximation (T_c^0). It also predicts the onset of a region of short-range order over the broad temperature range $T_c<T<T_c^0$ It furthermore predicts a dependence of the nature of the transition on the dimensionality of the system, which is not present in the mean-field approximation.

2. Let us examine the model of a narrow-gap layered semiconductor with a symmetric, anisotropic spectrum of electrons and holes:

$$E_{1,2}(\mathbf{k})=\pm\left(\frac{E_g}{2}+\frac{\mathbf{k}_\parallel^2}{2m_\parallel}+\frac{\mathbf{k}_\perp^2}{2m_\perp}\right). \tag{1}$$

Here $\mathbf{k}_{\parallel,\perp}$ are the quasimomenta along and across the layers, $m_{\parallel,\perp}$ are the corresponding effective masses, and we are using the approximation $m_\parallel/m_\perp \ll 1$ everywhere, unless otherwise specified. We assume that the condition for an exciton instability, $\theta>0$, holds. The phase of the order parameter is strictly fixed; i.e., the interaction involving an interband transition of quasiparticles is not small in comparison with the density–density interaction,[2] and there is no soft (Goldstone) mode of collective excitations. We consider temperatures $T\ll T_c^0$ and we assume that the "weak-coupling condition" $\Theta\ll 1$ holds. We restrict the discussion to the static version of the self-consistent fluctuation theory.[4] We write the thermodynamic potential of the model, normalized to the state density, as follows:

$$\Omega=\sum_{\mathbf{q}} \alpha_{\mathbf{q}}\Delta_{\mathbf{q}}\Delta-\mathbf{q}+\beta\sum_{\mathbf{q},\mathbf{q}',\mathbf{q}''} \Delta_{\mathbf{q}}\Delta_{-\mathbf{q}'}\Delta_{\mathbf{q}''}\Delta_{\mathbf{q}'-\mathbf{q}-\mathbf{q}''}, \tag{2}$$

where $\Delta_{\mathbf{q}}$ is a Fourier component of the order parameter describing the electron–hole pairing,[1] we have $|\Delta_{\mathbf{q}}|\ll E_g$, and the coefficients $\alpha_{\mathbf{q}}$ and β are independent of the temperature at $T\ll T_c^0$. A distinctive feature of functional (2) is that we have $\alpha_{\mathbf{q}=0}<0$ and $\beta>0$. Specifically, in our case we have

$$\alpha_{\mathbf{q}}=-\Theta+\gamma_\parallel \mathbf{q}_\parallel^2+\gamma_\perp \mathbf{q}_\perp^2, \quad \gamma_\parallel=\frac{1}{4m_\parallel E_g},$$
$$\gamma_\perp=\frac{1}{4m_\perp E_g}, \quad \beta=\frac{1}{2E_g^2}. \tag{3}$$

Because of this distinctive feature, expression (2) is substantially different from the standard Ginzburg–Landau functional for a system with a second-order phase transition. In this case $\alpha_{\mathbf{q}=0}$ changes sign at the point of the transition.

To analyze functional (2), we follow the approach of Ref. 5. Specifically, we single out the average component $\langle\Delta\rangle$ and we set $\Delta(\boldsymbol{\rho})=\langle\Delta\rangle+\delta\Delta(\boldsymbol{\rho})$, where $\delta\Delta(\boldsymbol{\rho})$ is a fluctuation of the order parameter at the point $\boldsymbol{\rho}$. We construct a Gaussian approximating functional:

$$\Omega_{app}=-\Theta\langle\Delta\rangle^2+\beta\langle\Delta\rangle^4+\sum_{\mathbf{q}} (\alpha_{\mathbf{q}}+6\beta\langle\Delta\rangle^2+A)\delta\Delta_{\mathbf{q}}^2+B\beta\langle\delta\Delta^2\rangle^2. \tag{4}$$

The coefficients A and B are to be determined. The average is to be taken over configurations of functional (4). From the conditions for minimization and convexity of the functionals Ω and Ω_{app} we find one obvious relation:

$$A=(3-B)\beta\langle\delta\Delta^2\rangle. \tag{5}$$

A second necessary relation is found from the self-consistency equation for the static component of the generalized susceptibility,[5] $\chi_{\mathbf{q}}(T)$:

$$A=6\beta\langle\delta\Delta^2\rangle\left[1+\frac{\langle\Delta\rangle}{\langle\delta\Delta^2\rangle}\frac{\partial\langle\delta\Delta^2\rangle}{\partial\langle\Delta\rangle}\right], \tag{6}$$

with the known thermodynamic expression $\langle\delta\Delta^2\rangle=T\Sigma_{\mathbf{q}}\chi_{\mathbf{q}}(T)$. The equilibrium values of $\langle\Delta\rangle$ and $\langle\delta\Delta^2\rangle$ can be found from the system of equations

$$\langle\Delta\rangle[-\Theta+2\beta\langle\Delta\rangle^2+6\beta\langle\delta\Delta^2\rangle]=0, \tag{7}$$

$$\langle\delta\Delta^2\rangle=\frac{T}{2}\sum_{\mathbf{q}}[\alpha_{\mathbf{q}}+6\beta\langle\Delta\rangle^2+A]^{-1}, \tag{8}$$

where A is given by (6). Solving Eq. (8), a nonlinear differential equation, generally requires numerical methods. Nevertheless, we can draw several important conclusions without going through such calculations. We first determine the existence of the normal phase with $\langle\Delta\rangle\equiv 0$ in a purely 2D case. The static generalized susceptibility $\chi_0(T)$ is found for this case from the equation

$$\chi_0^{-1}=-2\Theta+\frac{T}{T_0}\ln\frac{\chi_0^{-1}+\zeta}{\chi_0^{-1}}, \quad \zeta=\frac{2W}{E_g}, \tag{9}$$

where $T_0=2\pi\gamma_{\parallel}/3\beta$, and W is the limiting energy of electron–hole excitations (in order of magnitude we have $W\sim E_g\Theta\ll E_g$, and this energy is independent of the temperature in our problem). Under the condition $T\ll W$, T_0, we find from (9)

$$\chi_0^{-1}(T)=\zeta\exp(-2\Theta T_0/T). \tag{10}$$

At "high" temperatures ($W\ll T\ll T_0$) we find

$$\chi_0^{-1}(T)=\left(\frac{T}{T_0}\zeta\right)^{1/2}. \tag{11}$$

Consequently, a normal phase with $\langle\Delta\rangle\equiv 0$ can exist over the entire temperature range down to $T=0$, and the reciprocal susceptibility χ_0^{-1} never vanishes. In the case of a quasi-2D system (in which the mass $m_\perp$ is not infinite), the temperature dependence $\chi_0^{-1}(T)$ begins to deviate from (10) at low temperatures, and χ_0^{-1} crosses zero at T', going negative at $T<T'$. A normal phase can thus exist only at $T>T'$. A qualitative estimate yields $T'\sim\Theta T_0(\delta/\zeta)^{1/2}$ under the conditions $\delta=m_{\parallel}/m_\perp\ll\zeta\ll 1$.

At the same time, the ground state at $T=0$ is characterized by a nonvanishing value $\langle\Delta\rangle(T=0)=(\Theta/2\beta)^{1/2}$, as can be clearly seen by analyzing functional (3). In other words, an exciton phase, the most favorable phase, exists. In the mean-field theory, the $\langle\Delta\rangle(T)$ dependence is a monotonic decrease, and zero is reached at $T=T_c^0$ at which $\chi_0^{-1}(T)$ simultaneously changes sign. The situation in our case is more complicated. The results of a numerical solution of system (5)–(7) for the 2D case ($m_\perp\to\infty$) and quasi-2D

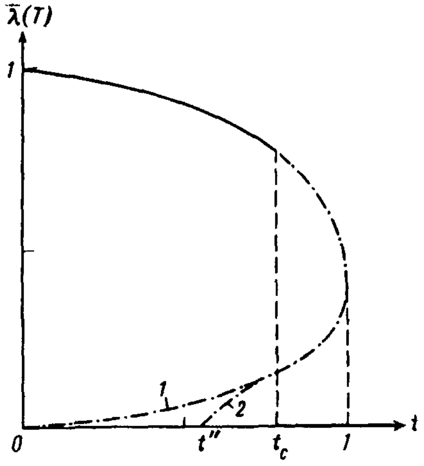

FIG. 1. Average value $\langle\Delta\rangle(T)$ versus the temperature. Solid curve—Stable phase; dot-dashed curve—metastable phase. 1) 2D case; 2) quasi-2D case. $t=T/T'$, $t_c=T_c/T'$, $t''=T''/T'$, $\bar{\lambda}(T)=[\langle\Delta\rangle(T)/\langle\Delta\rangle\times(0)]^2$.

case $(m_{\parallel}/m_{\perp}\ll 1)$, carried out over a broad range of parameter values, are shown qualitatively in Figs. 1 and 2 [also shown here are plots of $\langle\Delta\rangle(T)$ and $\langle\delta\Delta^2\rangle(T)$]. Some general conclusions follow from these calculations:

1. An exciton phase exists below a certain temperature T'', where the solution $\langle\Delta\rangle\neq 0$ arises abruptly, in the interval $0<T<T''$.
2. A normal phase exists above $T'<T''$, and in the purely 2D case we have $T'\to 0$.
3. The thermodynamic potentials of the two phases become equal at the temperature T_c, $T'<T_c<T''$. Consequently, T' and T'' are the temperatures of the supercooling and superheating, and T_c is the temperature of a first-order transition from the normal phase to the exciton phase.

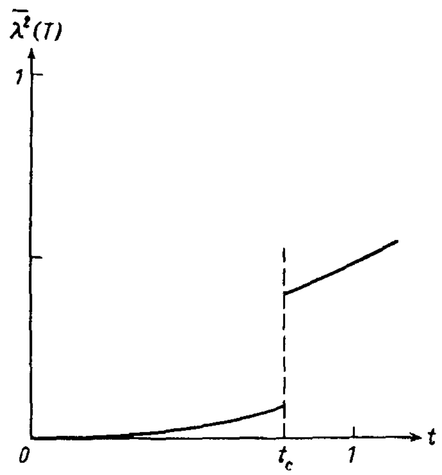

FIG. 2. The mean square fluctuation $\langle\delta\Delta^2\rangle(T)$ versus the temperature in the 2D case for the stable phase. $\bar{\lambda}(T)=\langle\delta\Delta^2\rangle(T)/[\langle\Delta\rangle(0)]^2$.

In order of magnitude we have T_c, $T'' \sim \Theta T_0 \sim \Theta E_g \ll T_c^0$. In the region $T_c < T < T_c^0$ there is a short-range order, and the temperature dependence $\chi_0^{-1}(T)$ [or, equivalently, $\langle \delta\Delta^2 \rangle (T)$] is given by equations like (10) and (11), with a replacement of the exponential behavior by a power-law behavior.

Finally, we take a brief look at the 3D case ($m_\parallel = m_\perp = m$). The expressions for the coefficients $\alpha_{\mathbf{q}}$ and β in terms of microscopic parameters in this case are only slightly different from (3); we will not reproduce them here. A main conclusion which follows from an analysis of (5)–(7) is that the transition to the exciton phase is a second-order transition at temperatures $T_c = T' = T'' \sim \Theta^{1/2} T_0$, at which the reciprocal susceptibility $\chi_0^{-1}(T)$ simultaneously vanishes. In the temperature interval $T_c < T < T_c^0$ there is a short-range order, characterized by a nearly linear $\chi_0^{-1}(T)$ dependence.

Some real systems, in which the exciton effects discussed above might play an important role, are heterostructures and superlattices based on certain III–V compounds and narrow-gap IV–V semiconductors. In a heterostructure of the GaSb–InAs–GaSb type with a wide InAs layer, the GaSb valence band overlaps the InAs conduction band.[6] In other words, the seed one-electron spectrum of the structure is gapless (semimetallic) in this case. However, this overlap can easily be eliminated by quantum-size effects for InAs layers with a thickness less than 85 Å or by a shift of the edge of the conduction band upon doping of the indium arsenide interlayer with (for example) aluminum. In the case of interest here, the width of the band gap must be less than or on the order of 0.01 eV; the corresponding thickness of the InAs interlayer would be 75–85 Å . In advanced molecular beam epitaxy, the required tuning of the width of the band gap of the structure can be achieved by either method (either by varying the thickness of the layers or by varying their composition), for systems based on either III–V or IV–VI compounds.

The onset of an exciton phase is known[1] to lead to a renormalization of the matrix elements for the interaction of quasiparticles with external fields. This renormalization may be manifested, in particular, by the onset of structural features in optical spectra, in the spin-relaxation time, etc., as the temperature is varied ("coherence effects," which have analogs in superconductivity). In addition, at the point of the transition to the exciton phase we would expect a surge on the temperature dependence of the derivative of the conductivity with respect to the temperature, since at this point the width of the band gap in a one-particle spectrum of the structure increases abruptly in the case of a first-order phase transition.

According to Ref. 7, a condensation of indirect excitons in structures based on GaAs/AlAs has recently been observed experimentally through changes in photoluminescence spectra in a magnetic field at low temperatures ($T < 4$ K).

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