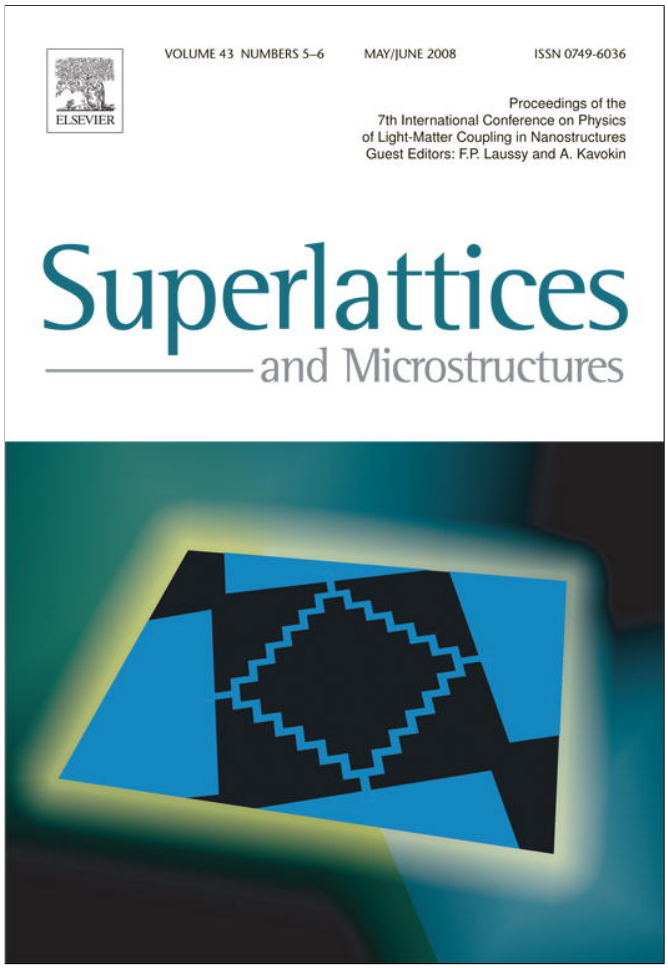

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On the possibility of excitonic phases at the semiconductor–semimetal transition

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Abstract

Motivated by recent experimental evidences for pressure-induced exciton condensation in intermediate valent Tm[Se,Te] compounds, we re-examine, adopting a BEC–BCS crossover scenario, the formation and stability of exciton insulator versus electron–hole liquid phases.

Keywords: Excitonic insulator; Electron–hole liquid; BEC–BCS transition

1. Motivation

The possibility of an excitonic insulator (EI)—understood as a macroscopic, phase coherent quantum state (exciton condensate) separating, below a critical temperature, a semiconductor (SC) from a semimetal (SM), has been anticipated by theorists about four decades ago [1]. Depending on, from which side of the SC–SM transition the EI is approached, the EI typifies either a Bose–Einstein condensate (BEC) of tightly bound excitons or a BCS condensate of loosely bound electron–hole pairs (see Fig. 1). In a series of experiments, Wachter and coworkers compiled strong evidence for excitonic phases in the vicinity of the pressure-induced SC–SM transition in intermediate valence $TmSe_{0.45}Te_{0.55}$ [2]. In particular, the anomalous increase in the electrical resistivity in a narrow pressure range around 8 kbar indicated the appearance of a new phase below 250 K. The experimentalists suggested that this phase may be an EI and, assuming pressure to modify only the energy gap E_g, constructed a phase diagram in the E_g–T

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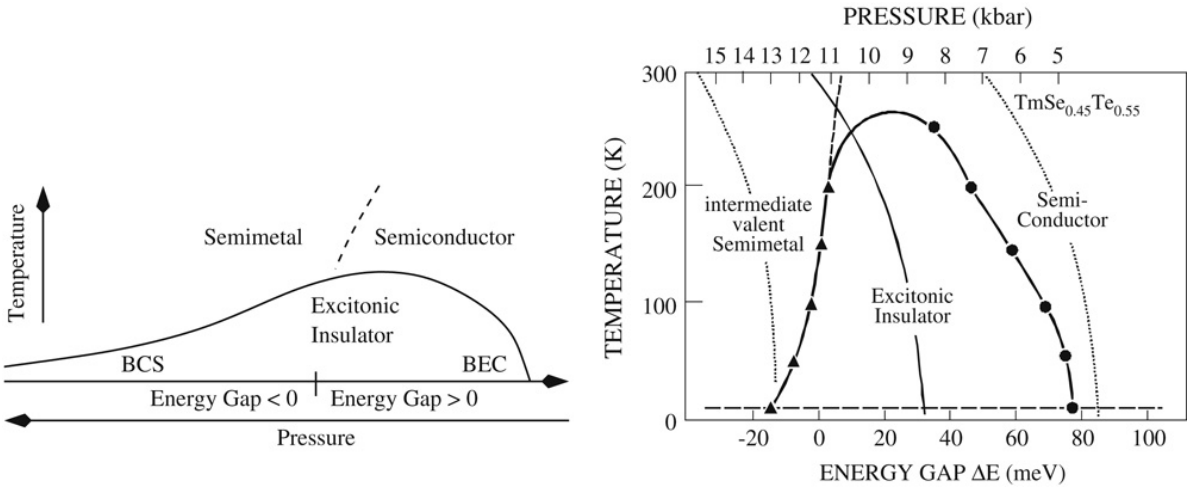

Fig. 1. Left panel: Sketch of the phase boundary of an EI with equal band masses. Right panel: Te[Se,Te] phase diagram deduced from $\rho(p, T)$ data (taken from Ref. [2]).

plane (Fig. 1, right panel) [2]. Later, the same group found in Tm[Se,Te] a linear increase in the thermal diffusivity below 20 K and related this to a BEC [3]. The interpretation of these data is however not straightforward and it is one of our goals to analyse the situation from a theoretical point of view.

2. Model

We start from an effective mass, Wannier-type model for electrons in the lowest conduction band (CB) and holes in the highest valence band (VB). The excitonic instability is driven by the Coulomb interaction which leads to a pairing of CB-electrons and VB-holes. Of particular importance is therefore to selfconsistently determine its weakening when pressure pushes the material from the SC side, with only a few thermally excited charge carriers available for screening, to the SM side, with a huge number of charge carriers. As long as the Coulomb interaction is strong enough to support excitons the material is on the SC side. The vanishing of the binding energy (Mott effect) then defines the SC–SM transition.

3. Method

Within the quasi-static plasmon-pole approximation the CB-electron ($i = 1$) and VB-hole ($i = 2$) selfenergies,

$$\Sigma_i(\mathbf{k}) = \Sigma_i^{sx}(\mathbf{k}) + \Sigma_i^{ch}(\mathbf{k}),$$

leading to a renormalisation of the bare energy bands $\epsilon_i(\mathbf{k}) = \mathbf{k}^2/2m_i$, are

$$\Sigma_i^{sx}(\mathbf{k}) = -\sum_{\mathbf{k}'} V_s(\mathbf{k}-\mathbf{k}')n_{\mathrm{F}}(\epsilon_i(\mathbf{k}') - \mu_i) \text{ (exchange energy)},$$

and

$$\Sigma_i^{ch}(\mathbf{0}) = \frac{1}{2}\sum_{\mathbf{k}'}[V_s(\mathbf{k}') - V_0(\mathbf{k}')] \text{ (Coulomb-hole)}.$$

The statically screened Coulomb potential

$$V_s(\mathbf{q}) = V_0(\mathbf{q})/\varepsilon(\mathbf{q}, 0),$$

with $V_0(\mathbf{q}) = 4\pi e^2/\varepsilon_0 q^2$ and

$$\varepsilon(\mathbf{q},\omega)^{-1} = 1 + \omega_{pl}^2 \left[(\omega + i0^+)^2 - \omega_{pl}^2 \left[1 + \left(\frac{q}{q_s} \right)^2 \right] - C \left(\frac{q^2}{4m_1} + \frac{q^2}{4m_2} \right)^2 \right]^{-1},$$

is constructed in such a way that sum rules are satisfied. Note that both, screening wave number

$$q_s = \left[\frac{4\pi e^2}{\varepsilon_0} \left(\frac{\partial}{\partial \mu_1} n_1 + \frac{\partial}{\partial \mu_2} \bar{n}_2 \right) \right]^{1/2}$$

and plasma frequency

$$\omega_{pl} = \left[\frac{4\pi e^2}{\varepsilon_0} \left(\frac{n_1}{m_1} + \frac{\bar{n}_2}{m_2} \right) \right]^{1/2},$$

depend on the CB-electron ($n_1 = g_1 \sum_{\mathbf{k}} n_{\mathrm{F}}(\epsilon_1(\mathbf{k}) - \mu_1)$) and VB-hole ($\bar{n}_2 = g_2 \sum_{\mathbf{k}} n_{\mathrm{F}}(\epsilon_2(\mathbf{k}) - \mu_2)$) densities, and have to be determined selfconsistently. Here n_F denotes the Fermi function, and the g_i account for the number of equivalent valleys and spins. The main effect of the selfenergies Σ_i is a rigid, $\mathbf{k}$-independent shift of the $\epsilon_i(\mathbf{k})$, resulting in a bandgap renormalisation $E_g \to \bar{E}_g$. This has been anticipated by auxiliary chemical potentials μ_i. By construction $\mu_1 + \mu_2 = -\bar{E}_g$. Then, the bare energy gap E_g, experimentally controlled via pressure, is given by $E_g = \bar{E}_g - \Sigma_1(0) - \Sigma_2(0)$. Supplementing these two equations by the charge neutrality condition, $n_1 = \bar{n}_2$, results in a closed set of equations for μ_1, μ_2, and $\bar{E}_g$.

First, we ignore Σ_i^{ch} in Σ_i (static approximation [4]) and derive a gap equation

$$\Delta(\mathbf{k}) = \int \frac{\mathrm{d}\mathbf{k}'}{(2\pi)^3} V_s(\mathbf{k} - \mathbf{k}') \Delta(\mathbf{k}') [n_F(e_2(\mathbf{k}')) - n_F(e_1(\mathbf{k}'))] / [e_1(\mathbf{k}') - e_2(\mathbf{k}')]^{-1}$$

for the off-diagonal (in the band indices) selfenergy [5]. Its linearisation then gives the transition temperature $T_c(E_g)$. Because pressure directly controls the chemical potentials constrained by charge neutrality, this mean-field approach turns out to be sufficient not only on the SM (weak coupling) but also on the SC (strong coupling) side of the BEC–BCS crossover.

In a second step [5], still in the static approximation, we apply the Thouless criterion, which states that condensation of excitons occurs when the electron–hole T-matrix diverges for $\mathbf{q} \to 0$ and $\omega \to 0$, and verify that $T_c(E_g)$ obtained from the T-matrix basically agrees with the above mean-field result. From the normal phase electron–hole T-matrix we can also determine the ionisation degree of the normal phase and the temperature $T_M(E_g)$ above which excitons cease to exist. T_M is given by $\bar{E}_X(E_g, T_M) = 0$, where $\bar{E}_X$ is the exciton binding energy renormalised by screening and phase space filling.

In a third step [6], we finally employ the full selfenergy (quasi-static approximation [4]) in order to study the possibility of an electron–hole liquid competing with excitonic phases in materials where the band structure is multi-valleyed. The thermodynamics of this state is contained in the electron–hole pair chemical potential $\mu_{eh}(r_s, T)$ which depends on the pair density parameter r_s and the temperature T. In our case, $\mu_{eh} = -E_g$, and we first have to determine $r_s(E_g, T)$ and then convert this relation into $-E_g(r_s, T)$. Comparing $-E_g(r_s, T)$ with the exciton binding energy and analysing for fixed T its r_s-dependence enables us to determine the region in the E_g–T plane where the electron–hole liquid may be favoured over excitonic phases.

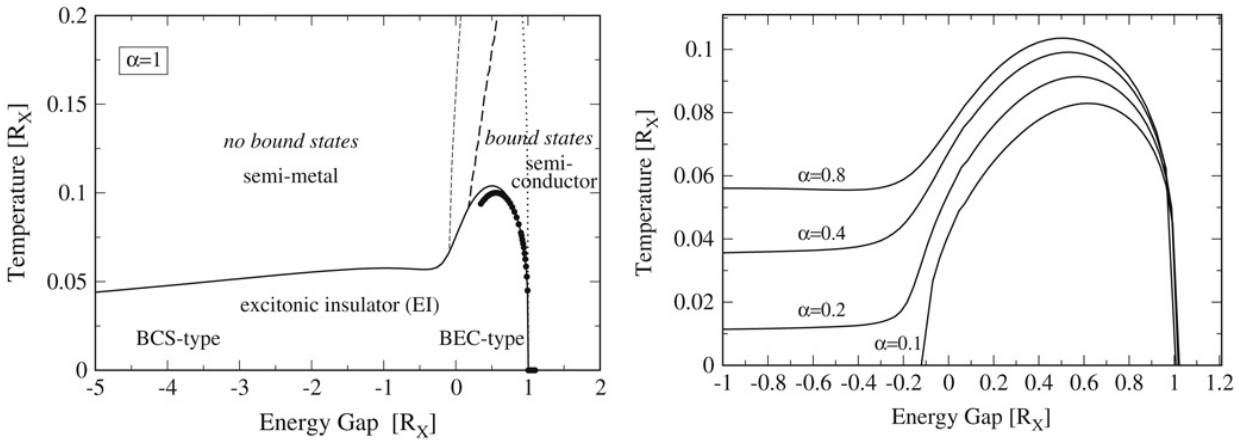

Fig. 2. Left panel: Phase boundary of an EI with equal band masses. The solid line (full circle) denotes T_c obtained from the linearised gap equation (Thouless criterion for BEC). The dotted line shows part of the phase boundary on the SC side when no screening due to thermally excited charge carriers is taken into account. The thick (thin) dashed line indicates the SC–SM transition, defined by the vanishing of the renormalised (screened) binding energy, taking screening and Pauli blocking (only screening) into account. Right panel: Phase boundaries for $\alpha > 0$. If $\alpha \ll 1$, the EI is strongly suppressed on the SM side because the chemical potentials for CB-electrons and VB-holes are different leading to breaking of Cooper-type electron–hole pairs. On the SC side, on the other hand, transition temperatures are only moderately reduced because of the $1/(m_1 + m_2)$-dependence typical for BEC.

4. Results

In the numerical work, we measure energies and lengths in units of the exciton Rydberg $R_X = 1/2ma_X^2$ and Bohr radius $a_X = \varepsilon_0/me^2$, respectively. Then our model is completely specified by g_i and the effective mass ratio $\alpha = m_1/m_2$. For Tm[Se,Te], we have $g_1 = 6$, $g_2 = 2$ and the intermediate valence provides us, due to f–d hybridisation, with a narrow f-VB, i.e. with a large effective hole mass $m_h \simeq 30 \ldots 60m_e$. Also the indirect bandgap ($E_g \simeq 135$ meV) is of advantage for exciton formation (binding energy ∼75 meV) and condensation [2].

Let us first consider however the generic case $g_1 = g_2 = 1$. Fig. 2 displays the phase boundary of the EI in the E_g–T plane (left panel). Its steeple-like shape reflects the different character of the EI when it is approached from the SM or SC side: Deep on the SM side the EI constitutes a BCS condensate of loosely bound electron–hole pairs whose small binding energies determine the low T_c. In contrast, on the SC side, the EI is a BEC of tightly bound excitons. Note that the higher transition temperatures $T_c(E_g)$ on this side are not determined by the larger binding energy but by the temperature for which the $\mathbf{q} = 0$ exciton state becomes macroscopically occupied. The binding energies per se set only the scale for the SC–SM transition [7]. The different condensation mechanisms leading to the EI on the SM and the SC side, respectively, can be most clearly seen when the band masses are different because mass asymmetry has a pair breaking effect on Cooper-type electron–hole pairs, similar to the effect a magnetic field has on Cooper pairs in superconductors (right panel of Fig. 2).

Next we show the phase boundary for an EI with $\alpha = 0.0125$ together with contours of the bound state fraction of its enveloping exciton environment (see Fig. 3). Note that the ionisation degree approaches 0% before phase coherence is established. In the bound state dominated region, we expect electrical resistivity anomalies similar to the ones observed in $TmSe_{0.45}Te_{0.55}$ [2]. The bound state fraction γ indicates on which side of the chemical equilibrium $e + h \rightleftharpoons X$ the system is according to the mass action law [8]. At low temperatures and large energy gaps γ acquires a step-like shape. Here $\bar{E}_X \to E_X \to R_X$, $\bar{E}_g \to E_g$, and

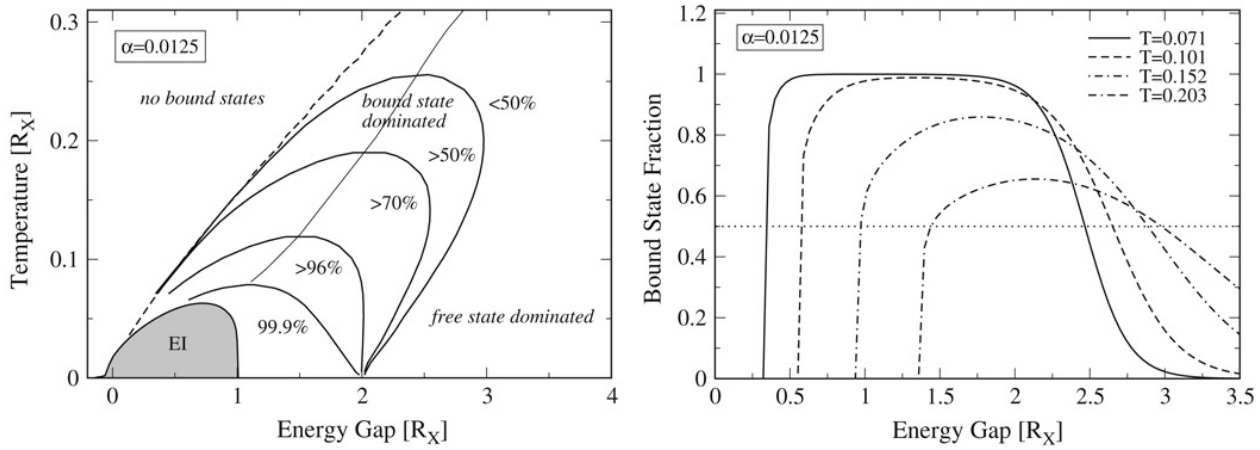

Fig. 3. Left panel: Phase boundary of an EI with $\alpha = 0.0125$ and contours where the bound state fraction γ is 99.9%, 96%, 70% or 50%. The thin solid line marks the temperature-dependent position of the maximum of γ. Right panel: Bound state fraction of the exciton matter above an EI. The interceptions with the dotted line indicate the energy gaps for $\gamma = 50\%$.

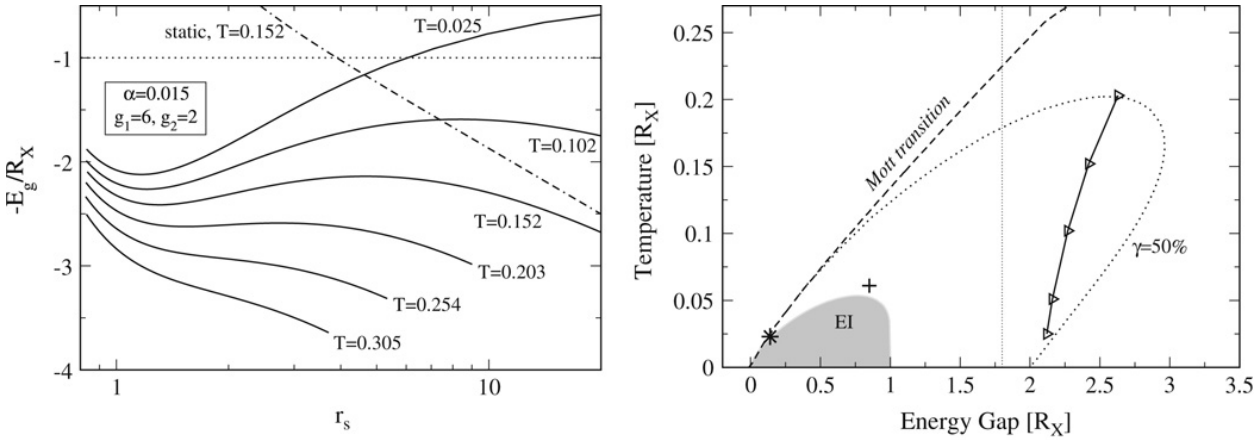

Fig. 4. Left panel: Electron–hole pair chemical potential $-E_g(r_s, T)$ as a function of electron–hole pair density parameter r_s. The dotted line indicates where the excitonic instability would occur at $T = 0$ and the dashed–dotted line gives $-E_g(r_s, T = 0.152)$ in the static approximation. Note that for $T < 0.254$, the isotherms go through a minimum. Right panel: Phase boundaries obtained for $TmSe_{0.45}Te_{0.55}$ parameters. Beyond the dashed line excitons disappear because of the Mott effect and the grey region denotes the EI. The thick dotted line is the 50%-contour of the bound state fraction. At the star the linear increase in the thermal diffusivity has been experimentally found [3] and at the plus symbol $n_1^b \approx 1.3 \times 10^{21}$ cm^{-3} is in good agreement with the experimentally estimated exciton density 3.9×10^{21} cm^{-3} [2]. The triangles are the points where $-E_g(r_s, T)$ goes through the minimum. The energy gap of $TmSe_{0.45}Te_{0.55}$ at ambient pressure is given by the vertical thin dotted line.

$\mu_1 \approx \mu_2 \approx -E_g/2$, leading to $\gamma \to 1 - \left[1 + (\frac{1+\alpha}{\alpha})^{\frac{3}{2}} \exp[\beta(R_X - E_g/2)]\right]^{-1}$. Thus γ jumps at $E_g = 2 \cdot R_X$ for $\beta E_g, \beta(E_g - R_X) \ll 1$.

We finally address for Tm[Se,Te] parameters the stability of the EI against an electron–hole liquid. Whereas in the static approximation $\bar{E}_g$ decreases monotonously with E_g for all T, the quasi-static approximation gives, for some E_g-range, a triple-valued $\bar{E}_g$ for $T < 0.254$. Because of the one-to-one correspondence between $\bar{E}_g$ and the pair density n, the system cannot choose a unique pair density. Fig. 4 shows that our model yields a coexistence region between the gaseous and the liquid phases. Anticipating the correct dilute limit, however, the usual Maxwell construction cannot be performed and the minimum simply indicates a jump in the pair densities,

that is, for large enough energy gaps the pair density n drops to zero. Of course, a gas–liquid transition and with it a coexistence region could only appear if the exciton binding energy is below the minimum of the chemical potential. In that case, excitons would be stable in a certain range. Since in our case the minimum of the pair chemical potential $-E_g(r_s, T)$ is below the exciton Rydberg, Wannier-type model excitons and thus excitonic phases (exciton gas, excitonic insulator) are unstable against a metallic phase. Anticipating, in addition, the decrease in the exciton binding energy with increasing density, the metallic phase would be in fact favoured over most of the relevant parameter ranges discussed so far. This can be seen if we combine the points where $-E_g(r_s, T)$ is minimal with the phase boundary of the EI, the (50%) contour of the bound state fraction, and the Mott line.

5. Summary

We investigated recent experimental claims for exciton condensation in $TmSe_{0.45}Te_{0.55}$. A VB-hole CB-electron mass asymmetry strongly suppresses the EI phase on the SM side, as observed experimentally. We found strong indications, however, that the phase boundary constructed from the electrical resistivity anomaly is not that of a coherent EI quantum condensate. The maximum in the resistivity could be instead caused by strong exciton-electron and exciton-hole scattering, in connection with pronounced intermediate valence effects. Furthermore, the analysis of the pair chemical potential suggests excitons in that region to be unstable against a metallic electron–hole plasma. Thus only if the exciton binding energy is pushed below the minimum of the metallic chemical potential, e.g. by phonon dressing or coherent intervalley scattering, the EI instability might occur in Tm[Se,Te].

Acknowledgments

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