Exciton Condensation in Tm[Se,Te] Compounds

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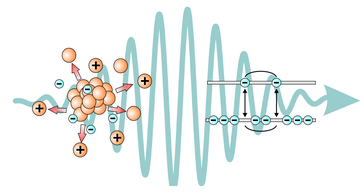

Abstract

Based on a two-band model for valence and conduction band electrons interacting via a screened Coulomb potential, we calculate the critical temperature below which exciton condensation occurs at the pressure-induced semiconductor-semimetal transition. In the spirit of a BCS-BEC crossover, we derive equations which determine, as a function of the energy gap (pressure), the chemical potentials for the two bands, the screening wave number, and the critical temperature. We show that on the semiconductor side the critical temperatures obtained from the linearized BCS gap equation coincide with the transition temperatures for BEC of non-interacting bosons, demonstrate that mass asymmetry strongly suppresses BCS-type pairing, and discuss experimental claims for exciton condensation in Tm[Se,Te] compounds.

Motivation

The possibility of an excitonic insulator (EI), separating, below a critical temperature, a semiconductor (SC) from a semimetal (SM), has been anticipated by theorists more than three decades ago [1]. Yet, experimental efforts to establish this phase in actual materials largely failed. It is only until recently, that experimental investigations of the SC-SM transition in $\mathrm{TmSe_{0.45}Te_{0.55}}$ suggested the existence of an EI phase in this compound [2, 3].

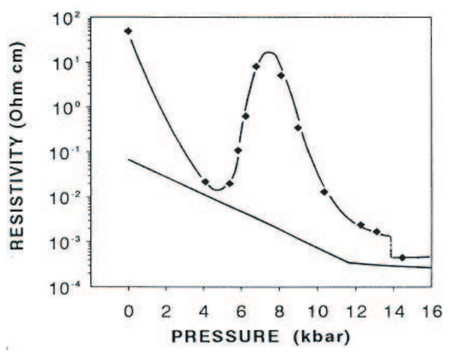

Fig 1: Pressure dependence of the electrical resistivity of $\mathrm{TeSe_{0.45}Te_{0.55}}$ *for T=4.2K (upper curve) and T=300K (lower curve). Data from Ref. [2].*

The anomalous increase of the electrical resistivity in a narrow pressure range around 8 kbar, for instance, indicated the appearance of a new phase at almost room temperature [2]. The experimentalists suggested that this phase may be an EI and, assuming pressure to modify only the energy gap $\mathrm{E_g}$, constructed a phase diagram for $\mathrm{TmSe_{0.45}Te_{0.55}}$ in the $\mathrm{E_g}$-T plane [2].

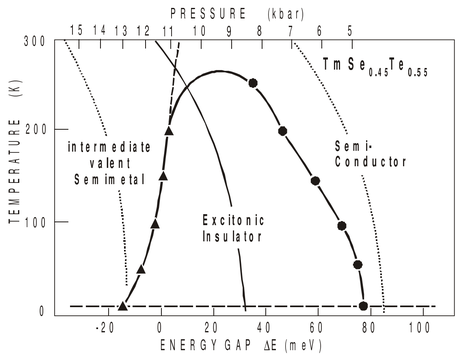

Fig 2: Phase diagram for $\mathrm{TeSe_{0.45}Te_{0.55}}$ *as obtained from the resistivity data [3].*

Later, the same group found in $\mathrm{TmSe_{0.45}Te_{0.55}}$ a linear increase of the thermal diffusivity below 20 K and related this to a condensate. The interpretation of the data is however not generally accepted, and it is one of our goals to analyze the experimental claims from a theoretical point of view.

Model

The EI arises because of the Coulomb attraction between electrons in the lowest conduction band (CB, i=1) and holes in the highest valence band (VB, i=2), with an indirect energy gap separating the two bands. Keeping only the dominant term of the Coulomb interaction and measuring momenta $\mathbf{k}$ from the respective extremata of the bands, an effective mass model for studying the (Wannier-type) EI is

$$H = \sum_{\mathbf{k},i} \mathrm{e}_i(\mathbf{k}) c^\dagger_{i,\mathbf{k}} c_{i,\mathbf{k}} + \frac{1}{2}\sum_{\mathbf{q}} V_s(\mathbf{q})\rho(\mathbf{q})\rho(-\mathbf{q}), \qquad (1)$$

with $\rho(\mathbf{q}) = \sum_{i,\mathbf{k}} c^\dagger_{i,\mathbf{k}+\mathbf{q}} c_{i,\mathbf{k}}$ the total charge density and $V_s(\mathbf{q}) = (4\pi e^2/\epsilon_0)/(q^2+q_s^2)$ the statically screened Coulomb potential. The screening wave number q_s depends on the CB electron and VB hole density and has to be determined selfconsistently; ϵ_0 is the background dielectric constant. Assuming isotropic effective masses m_i, the band dispersions are ($\hbar = 1$)

$$\mathrm{e}_1(\mathbf{k}) = \mathrm{E_g} + \varepsilon_1(\mathbf{k}) - \mu, \;\; \mathrm{e}_2(\mathbf{k}) = -\varepsilon_2(\mathbf{k}) - \mu - \Sigma_0(\mathbf{k}), \qquad (2)$$

with $\varepsilon_i(\mathbf{k}) = \mathbf{k}^2/(2m_i)$, and $\mathrm{E_g}$ the energy gap which can be varied continously through zero under pressure and μ the chemical potential. The band structure (2) refers to the unexcited crystal at T=0 with an empty CB and a full VB whose selfenergy $\Sigma_0(\mathbf{k})$ has to be therefore subtracted.

As far as the Tm[Se,Te] system is concerned, the model is of course rather crude, neglecting, for instance, strong intraband correlations, electron-phonon interactions, and the mixed valence. The two bands should be therefore considered as *effective single-particle bands* describing the electronic degrees responsible for the formation of an EI.

Method

We employ matrix propagators and derive, in the spirit of a BEC-BCS crossover, equations for the off-diagonal (in the band indices) selfenergy, the chemical potentials for CB electrons and VB holes, and the screening wave number. Because pressure directly controls the chemical potentials, which in turn are constrained by charge neutrality, the meanfield approximation turns out to be sufficient not only on the SM (weak coupling) but also on the SC (strong coupling) side. To determine the transition temperature $\mathrm{T_c(E_g)}$, we linearize the equations with respect to the off-diagonal selfenergy and map out the $\mathrm{E_g}$-T range in which it is finite. Using the Thouless criterion to deduce $\mathrm{T_c(E_g)}$ directly from the normal-phase electron-hole T-matrix, we explicitly verify that on the SC side $\mathrm{T_c(E_g)}$ coincides with the transition temperatures for BEC of non-interacting bosonic excitons. From the normal-phase electron-hole T-matrix we determine, moreover, the ionization degree of the normal phase and the temperature $\mathrm{T_M(E_g)}$ above which excitons cease to exist.

Calculation of $\mathrm{T_c(E_g)}$

In the meanfield approximation the selfenergy is given by the Fock diagram. After linearization we find

$$\Delta(\mathbf{k}) = \int \frac{d\mathbf{k}'}{(2\pi)^3} V_s(\mathbf{k}-\mathbf{k}') \frac{n_F(\bar{e}_2(\mathbf{k}')) - n_F(\bar{e}_1(\mathbf{k}'))}{\bar{e}_1(\mathbf{k}') - \bar{e}_2(\mathbf{k}')} \Delta(\mathbf{k}') \qquad (3)$$

for the off-diagonal selfenergy $\Delta(\mathbf{k}) = \Sigma_{12}(\mathbf{k})$ and

$$\Sigma_{ii}(\mathbf{k}) = -\int \frac{d\mathbf{k}'}{(2\pi)^3} V_s(\mathbf{k}-\mathbf{k}') n_F(\bar{e}_i(\mathbf{k}')) \qquad (4)$$

for the normal selfenergies. The single particle energies entering Eqs. (3) and (4) are the selfconsistent solutions of

$$\bar{\mathrm{e}}_i(\mathbf{k}) = \mathrm{e}_i(\mathbf{k}) + \Sigma_{ii}(\mathbf{k}). \qquad (5)$$

The main effect of the exchange energy on the particle dispersions is a rigid, k-independent energy shift which we incorporate into chemical potentials for the CB electrons and VB holes. Writing the renormalized dispersions as

$$\bar{\mathrm{e}}_i(\mathbf{k}) = (-)^i(\varepsilon_i(\mathbf{k}) - \mu_i) \qquad (6)$$

yields for the electron and hole chemical potentials

$$\mu_1 = \mu - \mathrm{E_g} - \Delta\mathrm{e}_1, \;\; \mu_2 = \Delta\mathrm{e}_2 - \mu, \qquad (7)$$

with energy shifts satisfying

$$\Delta\mathrm{e}_i = (-)^i \int \frac{d\mathbf{k}}{(2\pi)^3} V_s(\mathbf{k}) n_F(\varepsilon_i(\mathbf{k}) - \mu_i). \qquad (8)$$

To obtain a closed set of equations for the three unknown parameters, μ, μ_1, and μ_2, we augment the two equations in (7) by the condition of charge neutrality which forces the CB electron density n_1 to be equal to the VB hole density $\bar{n}_2$:

$$\int \frac{d\mathbf{k}}{(2\pi)^3} [n_F(\varepsilon_1(\mathbf{k}) - \mu_1) - n_F(\varepsilon_2(\mathbf{k}) - \mu_2)] = 0. \qquad (9)$$

With the individual chemical potentials for each species at our disposal, the screening parameter q_s is given by

$$q_s^2 = \frac{4\pi e^2}{\epsilon_0}\left(\frac{\partial}{\partial\mu_1} n_1 + \frac{\partial}{\partial\mu_2}\bar{n}_2\right) \qquad (10)$$

and the kernel of the BCS gap equation (3) is completely specified throughout the $\mathrm{E_g}$-T plane.

Calculation of the T-matrix and Thouless Criterion

For energies close to the exciton energy, the normal-state electron-hole T-matrix separates and can be calculated within a unitary-pole-approximation [4]. Introducing, $k_q = |\mathbf{k} - \frac{m_1}{M}\mathbf{q}|$ and $i\Omega_q = i\Omega_n + \mu_1 + \mu_2 - q^2/(2M)$, with $M = m_1 + m_2$, the T-matrix is given by

$$\Lambda_{12}(\mathbf{k},\mathbf{k}';\mathbf{q},i\Omega_n) = g(k_q)\cdot D(\mathbf{q},i\Omega_q)\cdot g(k_q), \qquad (11)$$

with an exciton propagator,

$$D(\mathbf{q},z) = \frac{-1}{z + B + M(\mathbf{q},z)}, \qquad (12)$$

defined in terms of a selfenergy,

$$M(\mathbf{q},z) = -\int \frac{d\mathbf{p}}{(2\pi)^3} \frac{[\frac{p^2}{2m}+B]^2}{\frac{p^2}{2m} - z} \chi^2(p) G(\mathbf{q},\mathbf{p}), \qquad (13)$$

and form factors $g(p)$ obtained from

$$g(p) = \int_0^\infty \frac{dp'p'^2}{4\pi^2} V_s(p,p')\chi(p') = [\frac{p^2}{2m} + B]\chi(p). \qquad (14)$$

Here, $V_s(p,p')$ is the angle averaged screened Coulomb potential, $m = m_1m_2/M$ and $G(\mathbf{q},\mathbf{p}) = n_F(\varepsilon_1(\mathbf{p}+\frac{m_1}{M}\mathbf{q}) - \mu_1) + n_F(\varepsilon_2(\mathbf{p} - \frac{m_2}{M}\mathbf{q}) - \mu_2)$ is a statistical factor describing Pauli-blocking. Replacing in Eq. (14) the screened Coulomb potential by the Hulthen potential, which is a good approximation on the SC side, where the screening parameter q_s is small, the form factors can be obtained analytically [4].

The pole of the exciton propagator (12) determines the analytical structure of the T-matrix. Physically, it gives the exciton binding energy $\bar{B}(\mathbf{q})$ renormalized by screening and phase-space-filling. Assuming a weak $\mathbf{q}$-dependence, $\bar{B}(\mathbf{q}) \approx \bar{B}(0) \equiv \bar{B}$, with

$$\bar{B} = B + \mathrm{Re}M(0, z \to -\bar{B} + i\eta). \qquad (15)$$

In terms of $\bar{B}$ the exciton propagator can be rewritten as

$$D(\mathbf{q},z) = \frac{-Z}{z + \bar{B}}, \qquad (16)$$

with an exciton spectral weight defined by

$$Z = 1 - \frac{\partial}{\partial\Omega}\mathrm{Re}M(0,\Omega + i\eta)|_{\Omega=-\bar{B}}. \qquad (17)$$

The Thouless criterion states that BEC of excitons occurs when the electron-hole T-matrix diverges for $\mathbf{q} = 0$ and $i\Omega_n = 0$. Using Eq. (11) this implies $D^{-1}(0,\mu_1+\mu_2) = 0$. With Eq. (16), the transition temperature $\mathrm{T_c(E_g)}$ is thus given by

$$\mu_1(\mathrm{E_g},\mathrm{T_c}) + \mu_2(\mathrm{E_g},\mathrm{T_c}) = -\bar{B}(\mathrm{E_g},\mathrm{T_c}), \qquad (18)$$

which is equivalent to the canonical criterion for BEC of a non-interacting Bose gas: The transition occurs when the chemical potential $\mu_X = \mu_1 + \mu_2$ of the bosons reaches the bottom of the band leading to a macroscopic occupation of the $\mathbf{q} = 0$ state.

Mott transition and ionization degree

As originally suggested by Mott, the SC-SM phase boundary is given by the temperature $\mathrm{T_M(E_g)}$ for which the exciton binding energy vanishes (Mott effect):

$$\bar{B}(\mathrm{E_g},\mathrm{T_M}) = 0. \qquad (19)$$

To obtain the ionization degree in the normal phase, we focus on the CB electron density (because of charge neutrality, we could as well target the VB hole density),

$$n_1 = \int \frac{d\mathbf{k}}{(2\pi)^2}\frac{d\omega}{2\pi} A_{11}(\mathbf{k},\omega) n_F(\omega), \qquad (20)$$

with the spectral function A_{11} obtained from the selfenergy in ladder approximation. Expanding A_{11} with respect to $\Gamma_{11} = \mathrm{Im}\Sigma_{11}$, Eq. (20) can be split into two parts, $n_1 = n_1^{\mathrm{f}} + n_1^{\mathrm{c}}$, with

$$n_1^{\mathrm{f}} = \int \frac{d\mathbf{k}}{(2\pi)^3} n_F(\varepsilon_1(\mathbf{k}) - \mu_1) \qquad (21)$$

the part of the total electron density corresponding to free electrons and

$$n_1^c = \int \frac{d\mathbf{p}}{(2\pi)^3} \int \frac{d\mathbf{q}}{(2\pi)^3} \left[\frac{B + \frac{p^2}{2m}}{\bar{B} + \frac{p^2}{2m}}\right]^2 \chi^2(p) F_1(\mathbf{p},\mathbf{q}), \qquad (22)$$

the part bound in electron-hole correlations (excitons); the statistical factor is given by $F_1(\mathbf{p},\mathbf{q}) = [n_F(E_X(\mathbf{q}) - \varepsilon_2(\mathbf{p} - \frac{m_2}{M}\mathbf{q}) + \mu_2) - n_F(\varepsilon_1(\mathbf{p} + \frac{m_1}{M}\mathbf{q}) - \mu_1)]\cdot[n_B(E_X(\mathbf{q})) + n_F(\varepsilon_2(\mathbf{p} - \frac{m_2}{M}\mathbf{q}) - \mu_2)]$.

The ionization degree can thus be defined as

$$\gamma = \frac{n_1^{\mathrm{f}}}{n_1^{\mathrm{f}} + n_1^{\mathrm{c}}}. \qquad (23)$$

Results

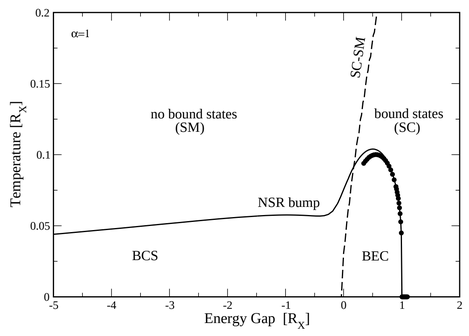

Fig 3: Phase diagram of an EI with equal band masses ($\alpha = 1$*).*

The phase boundary $\mathrm{T_c(E_g)}$ for an EI with equal band masses ($\alpha = m_1/m_2 = 1$) is presented in Fig. 3. Above T≈0.12, the EI is unstable and an ordinary SC-SM transition occurs (thick dashed line), here defined by the vanishing of the exciton binding energy $\bar{B}$. For T<0.12, a steeple-like phase boundary arises directly reflecting the different character of the EI when it is approached from the SM and SC side, respectively: On the SM side the EI constitutes a BCS condensate of loosely bound electron-hole pairs whose (small) binding energies determine the (low) transition temperatures. On the SC side, on the other hand, the EI is a BEC of strongly bound excitons. The (higher) transition temperatures $\mathrm{T_c(E_g)}$ coincide here with the temperatures for which the $\mathbf{q} = 0$ exciton state becomes macroscopically occupied (Thouless criterion (18); solid circles). The binding energies per se set only the scale for the SC-SM transition.

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 (Fig. 4). The chemical potentials for CB electrons and VB holes are then different for finite temperatures. 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. Accordingly, it leads to a strong suppression of $\mathrm{T_c(E_g)}$ on the SM side but not on the SC side, where the moderate α dependence of $\mathrm{T_c(E_g)}$ reflects the 1/M-dependence of the BEC transition temperature.

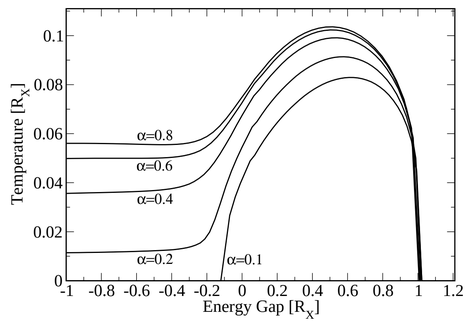

Fig 4: Phase boundaries for an EI as a function of $\alpha = m_1/m_2$*.*

For strong mass asymmetry the EI is almost entirely located on the SC side of the SC-SM boundary and is basically a BEC of excitons. Two temperatures are then required to characterize the EI: $\mathrm{T_M(E_g)}$ where exciton formation (*amplitude coherence*) sets in and $\mathrm{T_c(E_g)}$ where condensation (*phase coherence*) is finally reached. Above $\mathrm{T_c(E_g)}$ but below $\mathrm{T_M(E_g)}$, a mixture of excitons, free electrons, and free holes exists, the composition of which depends on T and $\mathrm{E_g}$, as can be seen in Fig. 5, where we plot the ionization degree above $\mathrm{T_c(E_g)}$ for an EI with $\alpha = 0.0125$, corresponding to $\mathrm{TmSe_{0.45}Te_{0.55}}$.

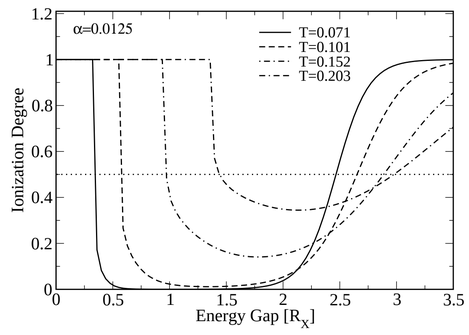

Fig 5: Ionization degree above $\mathrm{T_c(E_g)}$ *for an EI with* $\alpha = 0.0125$*.*

The phase boundary for an EI with $\alpha = 0.0125$ together with contours of the ionization degree of its enveloping exciton environment is displayed in Fig. 6. Note, the ionization degree approaches 0% *before* phase coherence is established.

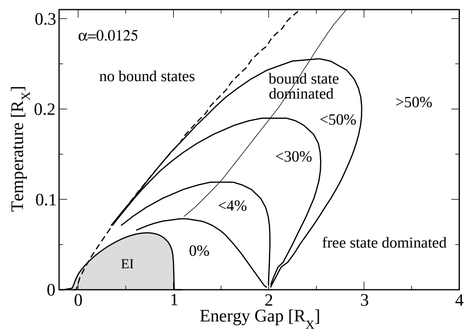

Fig 6: Phase boundary of an EI and contours of the ionization degree for $\alpha = 0.0125$*. The thin line denotes the minimum of the ionization degree.*

The resistivity anomaly observed in $\mathrm{TmSe_{0.45}Te_{0.55}}$ can be explained with the varying ionization degree of the excitonic matter when pressure pushes the system, above $\mathrm{T_c(E_g)}$ but below $\mathrm{T_M(E_g)}$, from the free state dominated to the bound state dominated regime (see Fig. 6). In the former, the resistivity is expected to decrease with pressure, because increasing pressure leads dominantly to an increase of free charge carriers. In the latter, however, increasing pressure dominantly leads to an increase of bound states accompanied by a relative freeze-out of free carriers and thus by an increasing resistivity. After a critical pressure, the freeze-out stops and the resistivity decreases again with pressure until it reaches the SC-SM transition where it changes abruptly to a lower value.

Phase coherence (condensation) is thus not necessarily required to explain the resistivity anomaly. Using $R_X = 75$ meV, the experimentally estimated exciton Rydberg for $\mathrm{TmSe_{0.45}Te_{0.55}}$, places the exciton rich region in the temperature range T∼50-250 K, exactly the range, where the anomaly has been observed. Phase coherence, on the other hand, we would expect below 50 K. Indeed, in Ref. [3] Wachter and coworker report a linear increase of the thermal diffusivity at around 20 K. From our theoretical perspective, this could be the long-sought EI.

Conclusions

We adopted a BEC-BCS crossover scenario to analyze recent experimental claims of exciton condensation in $\mathrm{TmSe_{0.45}Te_{0.55}}$. We found strong indications that the phase boundary constructed from electrical resistivity data is not the phase boundary of an EI. Instead, it embraces only the region where excitons dominate the total density (amplitude coherence). Our results suggests, however, that the EI (phase coherence) is very likely reached at the temperature scale where the linear increase of the thermal diffusivity has been found.

Discussions with Björn Hülsen, Dieter Ihle, Gerd Röpke and support from SFB 652 are greatly acknowledged.

References

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