Bound state formation and nature of the excitonic insulator phase in the extended 
Falicov-Kimball model

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Motivated by the possibility of pressure-induced exciton condensation in intermediate-valence 
Tm[Se,Te] compounds we study the Falicov-Kimball model extended by a finite f-hole valence band-
width. Calculating the Frenkel-type exciton propagator we obtain excitonic bound states above 
a characteristic value of the local interband Coulomb attraction. Depending on the system pa-
rameters coherence between c- and f-states may be established at low temperatures, leading to an 
excitonic insulator phase. We find strong evidence that the excitonic insulator typifies either a BCS 
condensate of electron-hole pairs (weak-coupling regime) or a Bose-Einstein condensate (BEC) of 
preformed excitons (strong-coupling regime), which points towards a BCS-BEC transition scenario 
as Coulomb correlations increase.

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That excitons in solids might condense into a macro-
scopic phase-coherent quantum state—the excitonic 
insulator—was theoretically proposed about more than 
four decades ago, for a recent review see Ref. 2. The 
experimental confirmation has proved challenging, be-
cause excitonic quasiparticles are not the ground state 
but bound electron-hole excitations that tend to decay 
on a very short timescale. Thus a large number of excitons 
has to be created, e.g. by optical pumping, with suf-

ficiently long lifetimes as a steady-state precondition for the 
Bose-Einstein condensate (BEC) realizing process.

The obstacles to produce a BEC out of the far-
off-equilibrium situation caused by optical excitation 
might be circumvented by pressure-induced generation 
of excitons. That pressure-sensitive, narrow-gap 
semiconducting materials, such as intermediate-valent 
TmSe0.45Te0.55, might host an excitonic BEC in solids 
came from a series of electric and thermal transport measurements.2 Fine-tuning the excitonic level, by 
applying pressure, to the level of electrons in the narrow 
4f-valence band, excitons can form near the semiconduc-
tor semimetal transition in thermodynamical equilibrium and 
might give rise to collective excitonic phases. A 
phase diagram has been deduced out of the resistivity, 
thermal diffusity and heat conductivity data, which con-

tains, below 20 K and in the pressure range between 5 
and 11 kbar, a superfluid Bose condensed state.2

The experimental claims for excitonic condensation in 
TmSe0.45Te0.55 have been analysed from a theoretical 
point of view.2,26 Adapting the standard effective-mass, 
(statically) screened Coulomb interaction model to the 
Tm[Se,Te] electron-hole system, the valence-band-hole 
conduction-band-electron mass asymmetry was found to 
suppress the excitonic insulator (EI) phase on the semimetallic side, as observed experimentally. But also 
on the semiconducting side, the EI instability might be 
prevented—within this model—by either electron-hole 
liquid phases2,24 or, at very large electron-hole mass ratios 
(\(\gtrsim 100\)), by Coulomb crystallization.2 The effective-mass 
Mott-Wannier-type exciton model neglects, however, im-
portant band structure effects, intervalley-scattering of 
excitons, as well as exciton-phonon scattering. Moreover, 
the excitons in Tm[Se,Te] are rather small-to-
intermediate sized bound objects (otherwise the experi-
mentally estimated exciton density of about 1.3 × 1021 
cm−3 would lead to a strong overlap of the exciton wave 
functions, see Refs. 2 and 4). Hence the usual Mott-
Wannier exciton description seems to be inadequate.

The onset of an EI phase was invoked quite recently in 
the transition-metal dichalcogenide 17-TiSe2 as driving 
force for the charge-density-wave (CDW) transition.2

The perhaps minimal lattice model capable of describ-
ing the generic two-band situation in materials being possible 
candidates for an EI scenario might be the Falicov-
Kimball model (FKM), introduced about 40 years ago in 
order to explain the metal-insulator transition in certain 
transition-metal and rare-earth oxides.2,11 In its original 
form the model introduces two types of fermions: itiner-
ant c (or d) electrons and localized f electrons with orbital 
energies εc and εf, respectively. The on-site Coulomb in-
teraction between c- and f-electrons determines the dis-
tribution of electrons between these “sub-systems”, and 
therefore may drive a valence transition as observed, e.g., 
in heavy-fermion compounds. To be a good model of the 
mixed-valence state, however, one should build in a co-
herence between c- and f-particles.2,12 This can be achieved 
by a c-f hybridization term V. Alternatively, a finite 
f-bandwidth, which is certainly more realistic than en-
tirely localized f-electrons, can also induce c-f coherence. 
The FKM with direct f-f hopping is sometimes called ex-
tended Falicov-Kimball model (EFKM).

Most notably, it has been suggested that a novel fer-
roelectric state could be present in the mixed-valence 
phase of the FKM with hybridization.2,26 The origin is 
a non-vanishing \((c^\dagger f)\) expectation value, causing a finite 
electrical polarization. In the limit V → 0 there is no fer-
roelectric ground state, as was shown in Refs. 13 and 14 in contrast to the findings in Ref. 12. Afterwards it has been demonstrated that spontaneous electronic ferroelectricity also exists in the EFKM, provided that the c- and f-bands involved have different parity. 15

By means of constrained path Monte Carlo techniques the \((T = 0)\) quantum phase diagram of the EFKM was calculated in the intermediate-coupling regime for one- and two-dimensional (2D) systems, confirming the existence of a ferroelectric phase. 16 A more recent 2D Hartree-Fock phase diagram of the EFKM 17,18 was found to agree surprisingly well with the Monte Carlo data, supporting mean-field approaches to the 3D EFKM (on the other hand the Hartree-Fock results have been questioned by a slave-boson treatment 19). The ferroelectric state of the EFKM can be viewed as an excitonic (on the other hand the Hartree-Fock results have been questioned by a slave-boson treatment 19). The ferroelectric state of the EFKM can be viewed as an excitonic condensate \((c^\dagger f)\) is an excitonic expectation value since \(f\) creates a f-band hole, i.e., the phase with non-vanishing polarization is in fact an EL phase.

Therefore, in this paper, we study the formation of excitonic bound states and the nature of the El phase in the framework of the (spinless) 3D EFKM. It can be written as

\[
H = \sum_{k\sigma} \varepsilon_{k\sigma} n_{k\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} ,
\]

where f- and c-orbitals are labeled by the pseudospin variable \(\sigma = \uparrow, \downarrow\) (or \(\sigma = \pm\)) with \(n_{k\sigma} = a_{k\sigma}^\dagger a_{k\sigma}\), \(a_{k\uparrow} \equiv f_{k}\), and \(a_{k\downarrow} \equiv c_{k}\). In Eq. (1), \(\varepsilon_{k\sigma} = \varepsilon_{\sigma} + t_{\gamma} \gamma_{k} - \mu\), \(\gamma_{k} = \frac{1}{2}(\cos k_{x} + \cos k_{y} + \cos k_{z})\), and \(\mu\) is the chemical potential. The signs of the transfer integrals \(t_{\gamma}\) determine the type of the gap for large enough \(|\varepsilon_{\uparrow} - \varepsilon_{\downarrow}|\) and/or \(U\) and of the electronic insulator (ferroelectric) state. Provided that \(t_{\gamma} t_{\downarrow} < 0\) we have a direct [indirect] gap and the possibility of ferroelectricity (FE) [antiferroelectricity (AFE)] with ordering vector \(Q = 0\) \(Q = (\pi, \pi, \pi)|\). In what follows, we put \(\varepsilon_{\downarrow} = 0\), \(\varepsilon_{\uparrow} > 0\), \(t_{\gamma} < 0\), \(t_{\downarrow} > 0\), and consider the half-filled band case \(\sum_{\sigma} n_{\sigma} = 1\), where \(n_{\sigma} = \langle n_{\sigma}\rangle = \frac{1}{N} \sum_{k} \langle n_{k\sigma}\rangle\)

First we investigate the existence of excitonic bound states in the phase without long-range order. To this end, we define the creation operator of a Frenkel-type exciton by

\[
b_{\sigma}^\dagger = a_{\sigma}^\dagger a_{\sigma}^\downarrow , \quad b_{\sigma}^\dagger = \frac{1}{\sqrt{N}} \sum_{k} a_{k+q\downarrow}^\dagger a_{k\sigma}^\downarrow ,
\]

and the exciton commutator Green function

\[
G_{X}(q, \omega) = \langle \langle b_{\sigma}^\dagger b_{\sigma}^\dagger \rangle \rangle_{\omega} .
\]

In the fermion representation of spins, we have \(b_{\uparrow}^\dagger = S_{\uparrow}, b_{\downarrow}^\dagger = S_{\uparrow}^\perp = (S_{\uparrow}^\dagger)^{+}\), so that \(G_{X}(q, \omega) = \langle \langle S_{\uparrow}^\dagger S_{\uparrow}^\dagger \rangle \rangle_{\omega}\) may be considered as the negative dynamic pseudospin susceptibility. Therefore, to obtain the exciton propagator \(G_{X}\), the calculation of the dynamic spin susceptibility in the Hubbard model 20 can be adopted. Taking the ruin-
Carlo phase diagrams for intermediate couplings\textsuperscript{17} might justify the application of the Hartree-Fock approach to values of the Coulomb attraction $U$ of the order of the bandwidth.

To make contact with previous Hartree-Fock approaches\textsuperscript{17,18}, we use the equation of motion method for the anticommutator Green functions\textsuperscript{20} $\langle a^\dagger_{k\sigma}a_{k\bar{\sigma}} \rangle\omega$ and $\langle a^\dagger_{k\sigma}a_{k\bar{\sigma}} \rangle\omega$, and perform a decoupling that allows for the description of the FE EI phase by the order parameter

$$\Delta = \frac{U}{N} \sum_k \langle a^\dagger_{k\uparrow}a_{k\downarrow} \rangle.$$ \hspace{1cm} (8)

We obtain $\langle a^\dagger_{k\uparrow}a_{k\downarrow} \rangle = \Delta \sum_\sigma \sigma f(E_{k\sigma})/(2E_k)$ with $E_{k\sigma} = \frac{1}{2}(\varepsilon_k + \varepsilon_k) - \sigma E_k$, $E_k = [\xi^2_k + \Delta^2]^{1/2}$, $\xi_k = \frac{1}{2}(\varepsilon_k - \varepsilon_k)$, and

$$\langle n_{k\sigma} \rangle = \frac{1}{2} \left[ 1 + \frac{\xi_k}{E_k} \right] f(E_k) + \frac{1}{2} \left[ 1 - \frac{\xi_k}{E_k} \right] f(E_k).$$ \hspace{1cm} (9)

Then, for $\Delta \neq 0$, we get the gap equation

$$1 = \frac{U}{N} \sum_k \sigma f(E_{k\sigma})/2E_k.$$ \hspace{1cm} (10)

Figure 1 shows the finite-temperature phase boundary of the EI phase obtained by the self-consistent solution of the Hartree-Fock Eqs.\textsuperscript{8,10,11} In comparison with the semielliptic DOS (solid line), the use of the more realistic tight-binding DOS (dashed line) yields a shrinking of the EI phase, which corresponds to the behavior of the boundary $U_X(T)$ for exciton formation. For $U > U_s$ we obtain the phase boundary $T_c(U)$ coinciding with the boundary $T_X(U)$ for exciton formation. This result gives a strong argument for the BEC of preformed (tightly bound) excitons at $T_c(U > U_s)$. On the other hand, for $U < U_s$ there are no preformed excitons above $T_c$, and a BCS-like condensation at $T_c(U < U_s)$ takes place, i.e., the pair formation and condensation occurs simultaneously. Although the gap equation captures the BCS and BEC situation at weak and strong couplings\textsuperscript{5,21,22}, it cannot discriminate between them.

Thus, the existence or non-existence of bound states above $T_c$ gives strong evidence for a BEC or BCS transition scenario at $T_c$, respectively. Moreover, within the EI phase, a crossover from a strong-coupling BEC to a weak-coupling BCS condensate of electron-hole pairs is strongly suggested.

To describe qualitatively this BEC-BCS crossover region, we consider the gap boundary $U_g(T)$ (thin dotted and dashed-dotted lines) resulting from $E_g^{(0)} = 0$ [Eq. 20], where the gap opens for $U > U_g$. Interestingly, at $T_c = T_c(U_g)$ we obtain $U_g(T_c) = U_X(T_c)$. That is, at this point the opening of the gap is accompanied with the formation of bound states, whereas for $T > T_c, U_g(T)$ is slightly smaller than $U_X(T)$. From this result we may get a crude estimate of the BEC-BCS crossover region by extrapolating $U_g(T)$ into the EI phase. Solving Eq. 20 at a fixed $T < T_c$, for $U$ in the region $U_g < U < U_X$ we get negative pole energies $\omega_X$ which indicates the instability of the normal phase with bound states against the long-range ordered EI phase. Moreover, for $U \lesssim U_g$ no solution can be found which may be indicative for an instability towards a BCS-type EI state. Thus, the BEC-BCS crossover in the EI phase should occur in the neighborhood of the $U_g(T)$ line.

In comparison to the phase boundary obtained within the simple effective-mass, Mott-Wannier-type model\textsuperscript{5,26} the EI phase of the EFKM is confined at zero temperature on the weak-coupling side, because of the finite f- and c-bandwidths. While the shape of the EI dome approximates the Ti[Te,Se] phase diagram constructed from the experimental data, the absolute transition temperatures are overestimated, of course, by any mean-field approach. The homogeneous EI phase shrinks as $\delta$ as $t_f$ becomes smaller at fixed $\delta$, but it does not disappear\textsuperscript{14}.

Figure 2 gives the partial f- and c-electron DOS at various characteristic points A-F of the phase diagram shown in Fig. 1. The high-temperature phase may be viewed as a metal/semimetal (panel A) or a semiconductor (panel B) in the weak- or intermediate-to-strong interaction regime, respectively. The EI phase shows completely different behavior. As can be seen from panel C, a correlation-induced “hybridization” gap opens, indicating long-range order (non-vanishing f-c-polarization). As
the temperature increases the gap weakens and finally closes at $T = T_c$. The pronounced $c$-f-state mixing and strong enhancement of the DOS at the upper/lower valence/conducting band edges is reminiscent of a BCS-like structure evolving from a (semi-) metallic state with a large Fermi surface above $T_c$ (see panel A). This may be in favor of a BCS pairing in the weak-coupling region of the EI phase, as discussed above. By contrast the DOS shown in panel D clearly evolves from a gapped high-temperature phase. Finally, in panel E [F] the partial $f$- and $c$-electron DOS at $T \approx 0$ below [above] the EI phase are depicted, where the system behaves as a metal or semimetal [band insulator or semiconductor]. Note that the splitting of $c$- and $f$-bands in panel F is not caused by $\delta$ (being the same as in E), but is due to the Hartree shift $\propto U(n_f - n_c)$.

To summarize, in this work, we attempted to link experimental hints for excitonic condensation to recent theoretical studies of electronic ferroelectricity in the extended Falicov-Kimball model. We analyzed the finite-temperature phase diagram and argued that a finite $f$-bandwidth in combination with a short-range interband Coulomb attraction between (heavy) valence-band holes and (light) conduction-band electrons may lead to $f$-$c$-band coherence and an excitonic insulator low-temperature phase. Most noteworthy, we established the existence of excitonic bound states for the EFKM on the semiconductor side of the semimetal semiconductor transition above $T_c$, and suggested a BCS-BEC crossover scenario within the condensed state. As a consequence, we expect pronounced transport anomalies in the transition regime both in the low- and high-temperature phases, which should be studied in the framework of the EFKM in future work.

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