Electron–hole instability in 1T-TiSe$_2$

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Abstract. In this paper, we address the question of the origin of the charge density wave instability in 1T-TiSe$_2$. We develop a model considering the direct Coulomb interaction between electrons and holes in the valence and conduction bands near the Fermi energy. Using the Bethe–Salpeter equation, we calculate the electron–hole correlator, which reveals an instability at low temperature leading to a transition toward a commensurate superstructure mediated by the electron–phonon coupling, in agreement with experiments. On the basis of this correlator, the electron self-energies are then calculated and the corresponding photoemission spectra are compared with the experimental ones, revealing good agreement. The signature of electron–hole fluctuations in photoemission is emphasized. Furthermore, we calculate the spectral function of the phonon mode, whose softening is experimentally observed at the transition.
1. Introduction

$1T$-TiSe$_2$ is one of the simplest and most widely studied transition metal dichalcogenides that undergo a transition to a charge density wave (CDW) state. It takes place around $T_c = 200$ K and leads to a commensurate $2 \times 2 \times 2$ superstructure [1]. Different aspects of this phenomenon—in particular, the static and dynamic behaviors of the crystal lattice [2–5] and the evolution of the electronic states [6–8]—have been investigated by many authors. The lattice superstructure is prepared by the softening of the lowest transverse phonon mode at the L points on the border of the Brillouin zone. The displacements of the ionic positions in the CDW phase correspond to the eigenvectors of this vibrational mode.

The electronic band structure near the Fermi energy is governed by two bands: a valence band, composed mainly of Se 4p states, with a maximum at the $\Gamma$ point, and a Ti 3d conduction band with minima at the L points. The electronic structure has been studied by band structure calculations using density functional theory [3, 9, 10]. Many-body effects have been incorporated, e.g. by the self-energy computed by Hedin’s GW approximation [11]. Depending on the method used, the final results for the detailed energy dependence of the two main bands are different: the compound can be a semi-conductor with a small indirect gap or a semi-metal with a small energy overlap between the two bands. On the experimental side many very detailed angle-resolved photoemission (ARPES) measurements have been carried out in order to present the electronic spectral functions of these bands [12–16]. Below $T_c$ they show interesting ‘backfolding’ effects of the CDW transition on the band states, but similar signs are also visible above $T_c$ in the undeformed lattice.

In spite of many years of intensive studies, the mechanism at the basis of this elementary CDW transition remains unclear. Different hypotheses have been proposed in order to understand the driving force: it could be the consequence of a Jahn–Teller effect [12, 17] or of the formation of an excitonic condensate [18, 19]. In the first case a commensurate spatial reconstruction of the lattice would lower the electronic energy close to the Fermi surface by facilitating charge transfer between neighboring 4p and 3d orbitals. In this case, the lattice transformation is—in a sense—the driving mechanism that leads to a different crystal structure.
that is energetically more favorable for the electrons. The excitonic scenario, on the other
hand, relies on the weakly screened Coulomb attraction between holes in the valence band and
electrons in the conduction band that favors the formation of bound electron–hole (e–h) states.
In this case the driving force is of electronic origin. The bound e–h pairs forming the excitonic
condensate below $T_c$ have a center-of-mass wave vector $\mathbf{w}$—equal to the vector between $\Gamma$
and the corresponding L point—which is not a reciprocal lattice vector of the undeformed
crystal. Therefore the electronic charge density has a periodicity different from that in the high-
temperature phase. This CDW then forces the underlying lattice to adapt to the new charge
structure. In both scenarios there is close cooperation between the electrons and the ionic lattice.
Thus a third hypothesis which invokes a combination of the two described above has more
recently been put forward [6, 20].

In previous work [8, 15, 21], we have presented photoemission spectra obtained by ARPES
measurements, and we have interpreted the spectra below $T_c$ in the framework of excitonic
condensation. In the condensed phase the creation operator for an e–h pair, given by the product
of an annihilation operator for a valence band state and a creation operator for a conduction
band state, has a non-vanishing average. A simple mean-field treatment proposed many years
ago for this phenomenon [22, 23] allows us to calculate the temperature dependence of this
average, which is the amplitude of the condensate, as well as the corresponding electronic
spectral functions. It turns out that this approach reproduces quite satisfactorily the measured
spectra, in particular the ‘backfolding’ of the conduction band pieces around the L points to
$\Gamma$ and—inversely—of the valence band from $\Gamma$ to the L points.

This success can be taken as a hint that excitonic effects indeed play an important role in
$1T$-TiSe$_2$. However, it is not a proof that this is the full explanation of the CDW phase. In these
calculations the lattice reconstruction is usually not taken into account. Two important effects
are therefore missing: this lattice deformation, by reducing the size of the Brillouin zone such
that $\mathbf{w}$ becomes a reciprocal lattice vector, can produce a backfolding effect on the electronic
spectral functions similar to that obtained by an exciton condensate. Moreover, one should treat
the formation and condensation of excitons in the distorted lattice structure. The cooperation
between electrons and the lattice should therefore be studied in more detail.

The purpose of this work is to take a step in this direction. We evaluate the strength of
e–h fluctuations at temperatures above the CDW transition and analyze their effect on the
electronic states and on the ionic lattice. In section 2, we present the type of Hamiltonian on
which our calculations are based. The coupling between electrons and ions is expressed in
terms of the tight-binding (TB) approach. This TB Hamiltonian has been used to calculate
the band structure [7], and when it is expanded in terms of lattice displacements, it
produces electron–phonon coupling [24]. A screened interband Coulomb interaction introduces
correlations between the states in the two bands. Using this Hamiltonian, we calculate three
important quantities in section 3: the e–h correlation function, the self-energies and spectral
functions of the electrons and the spectral function of the soft phonon mode. In section 4,
ARPES spectra measured in the undeformed lattice phase are shown that already reveal
backfolding effects that seem to anticipate what will happen below $T_c$. We compare the
measured spectra with the theoretical spectral functions. In the final section, we conclude by
summarizing the main results. We demonstrate the relevance of e–h correlations already above
the CDW transition. We also comment on the role e–h correlations may then play in the low-
temperature CDW phase of $1T$-TiSe$_2$, and we point out that further theoretical work should
be done in future to explain in detail the behavior below the CDW transition temperature, in
particular the ARPES spectra and phonon dispersions.

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2. Theoretical basis

We describe the properties of $1T$-TiSe$_2$ on the basis of the following Hamiltonian:

\[ H = H_0 + H_C + H_{EL}. \] (2.1)

$H_0$ determines the electron dispersion of the valence and the conduction bands:

\[ H_0 = \sum_k \varepsilon_v(k) a_v^\dagger(k) a_v(k) + \sum_{k,i} \varepsilon_c^i(k) a_c^{\dagger,i}(k) a_c^i(k). \] (2.2)

The operator $a_v^\dagger(k)$ creates an electron in the valence band, respectively the conduction band with momentum $k$ with respect to its extremum. We are mainly interested in its form near the band extrema. The valence band has its maximum at $\Gamma_1$ (the center of the Brillouin zone) where the dispersion has the form

\[ \varepsilon_v(k) = E_v - \frac{k^2}{2m_v}. \] (2.3)

The conduction band has three equivalent minima at the points $L_i$, which are linked with $\Gamma$ by the vectors $w_i$. The band energy near the $L$ point in the $x$-direction of the Brillouin zone (we call it $L_1$) has the form

\[ \varepsilon_c^1(k) = E_c + \frac{(k_x - w_{1x})^2}{2m_{cx}} + \frac{k_y^2}{2m_{cy}}. \] (2.4)

For the other two $L$ points the local reference axis is turned by $\pm 120^\circ$. $w_{1x}$ is the $x$-component of the wave vector $w_1$ linking $\Gamma$ and $L_1$. Appropriate values of the effective masses $m_v$, $m_{cx}$ and $m_{cy}$ and the energy offsets $E_v$ and $E_c$, determining the positions of the band extrema, will be chosen in the following section. In all our calculations we take the chemical potential as the zero of energy.

In the following calculations, we do not take into account the band dispersions in the $k_z$-direction. The (two-dimensional) Fermi surface consists of a symmetric paraboloid around $\Gamma$ for the valence band and an elliptic paraboloid around each minimum of the conduction bands, having the corresponding vector $w_i$ as its long axis.

$H_C$ contains the Coulomb interaction between electrons. We assume that Hartree and exchange terms have already been incorporated into the electronic band structure. Being mainly interested in the e–h interplay between the valence and the conduction band, we only include the Coulomb interaction between the two bands:

\[ H_C = \sum_q \rho_v(q) V_C(q) \rho_c^\dagger(q). \] (2.5)

$V_C(q) = e^2 (\varepsilon_0(q^2 + q_0^2))^{-1}$ is the screened Coulomb interaction acting between the charge densities $\rho_\lambda(q)$ of the two bands ($\lambda = v$ or $c$). In order to avoid heavy numerical work, in the following calculations we will replace $V_C(q)$ by a constant $V_0$, corresponding to a potential that is local in space. In this way, we will effectively treat a Hubbard, respectively an extended Falicov–Kimball-type model [29, 30] with a local repulsion between electrons in different bands. The choice of an appropriate value of $V_0$ will be discussed later.
The third term in (2.1), $H_{EL}$, contains the interaction between the electrons and the lattice. We start from a TB Hamiltonian

$$H_{TB} = \sum_{l,l'} \sum_{\mu \nu} \sum_{\alpha \beta} J_{\alpha \beta}(R_l + \tau_\mu + u(l, \mu) - R_l' - \tau_\nu - u(l', \nu)) \hat{c}^\dagger_{\alpha \mu}(l) \hat{c}_{\beta \nu}(l').$$  \hspace{1cm} (2.6)

Here $\{R_l\}$ are the coordinates of the elementary cells, the vectors $\tau_\mu$ determine the equilibrium positions of the ions in the cell and $u(l, \mu)$ are small displacements of the ions [2]. $J$ is the matrix of exchange integrals, determined by the local orbitals $\phi_\alpha$, located on the ion at $R_l + \tau_\mu$, and $c^\dagger$ and $c$ are the creation and annihilation operators for electrons on the corresponding lattice sites. Diagonalizing the exchange matrix without displacements $u(l, \mu)$ yields the band dispersions introduced above. Expanding the exchange integrals to first order in this lattice deformation, one obtains the electron–phonon interaction:

$$H_{EL} = \sum_{\lambda, \lambda', k} \sum_{q \alpha} g_{\lambda \lambda'}(k, q \alpha) a^\dagger_{\lambda \alpha}(k) a_{\lambda' \alpha}(k - q) Q(q \alpha),$$ \hspace{1cm} (2.7)

with $Q$ being the phonon amplitude of the vibrational mode $\alpha$ with wave vector $q$ and polarization vectors $e(\mu, q \alpha)$,

$$u(l, \mu) = \frac{1}{\sqrt{N M_\mu}} \sum_{q \lambda} e(\mu, q \alpha) \exp (i q \cdot R_\lambda) Q(q \alpha),$$ \hspace{1cm} (2.8)

and $g_{\lambda \lambda'}(k, q \alpha)$ are the coupling coefficients determining the interaction between the electronic bands $\lambda$ and $\lambda'$ and the phonon with wave vector $q$ in mode $\alpha$. The details can be found in [7, 24, 25].

On the basis of our Hamiltonian we want to focus on two aspects of the properties of 1T-TiSe$_2$ above the temperature of its lattice transformation: the spectral functions of the two electron bands and of the lowest transverse phonon mode. The results of our calculations, presented in section 3, will be compared with experimental data in section 4. Below we give more details of the subsequent calculations.

### 2.1. Electron self-energies

In order to capture the influence of the interband Coulomb interaction on the electronic spectral functions, we calculate the self-energies $\sigma_e$ and $\sigma_v$ of the valence and conduction electrons using their coupling to e–h fluctuations [31]. For a local potential they are given by the following expressions:

$$\sigma_v(p, z_\alpha) = -\frac{V_0^2}{(-i \beta)} \sum_{\beta} \sum_{Q,i} G'_v(p + w_i + Q, z_\beta) X_i(Q, z_\beta - z_\alpha),$$ \hspace{1cm} (2.9a)

$$\sigma_c(p + w_i, z_\alpha) = -\frac{V_0^2}{(-i \beta)} \sum_{\beta} \sum_{Q} G'_c(p - Q, z_\beta) X_i(Q, z_\alpha - z_\beta).$$ \hspace{1cm} (2.9b)

Here $G_v$ and $G'_c$ are the one-electron Green functions for the corresponding bands (for the conduction band the index $i$ distinguishes the regions around the $L_i$ points), $z_\alpha$ and $z_\beta$ are fermionic Matsubara frequencies and $X_i$ is the e–h correlation function

$$X_i(Q, z) = \sum_{p, p'} G_{2i}(Q, pp', z)$$ \hspace{1cm} (2.10)
related to the two-particle Green function \( G_2^i \) describing the behavior of pairs with center-of-mass momentum \( Q \) and relative momentum \( p \), formed by a hole in the valence band and an electron in the conduction band \( i \). For \( i = 1 \) it is defined, as a function of time, by

\[
G_2^1(Q, pp', t - t') = -\langle T[a_v^\dagger(P_v(p, Q), t)a_e^\dagger(P_e(p, Q), t)\alpha a_e^\dagger(P_e(p', Q), t')a_v(P_v(p', Q), t')]\rangle,
\]  

(2.11)

where

\[
P_v(p, Q) = (p_x - \alpha_{1x} Q_x, p_y - \alpha_{1y} Q_y),
\]

\[
P_e(p, Q) = (p_x + \alpha_{2x} Q_x + \omega_{1x}, p_y + \alpha_{2y} Q_y),
\]

\[
\alpha_{1x} = \frac{m_v}{M_v}; \quad \alpha_{1y} = \frac{m_v}{M_v}; \quad \alpha_{2x} = \frac{m_e}{M_v}; \quad \alpha_{2y} = \frac{m_e}{M_v}; \quad M_i = m_v + m_e.
\]

The functions for \( i = 2 \) and 3 have the same form, but \( p \) and \( Q \) are introduced with their coordinates with respect to a reference system oriented along the main axes of the corresponding Fermi surface paraboloid.

The electronic Green functions evaluated using the self-energies (2.9a) and (2.9b) have a similar form as those used in mean-field approximation for the phase in which an excitonic condensate exists [8, 15]. However, the interband coupling in (2.9a) and (2.9b) is created by e–h fluctuations, rather than by the excitonic condensate. Our results shown in section 3 demonstrate to what extent these fluctuations, which are already active above the condensation temperature, indeed anticipate and prepare the effect of the condensate.

2.2. Electron–hole (e–h) correlator

\( G_2^i \) is calculated with the help of the Bethe–Salpeter equation [33]

\[
G_2^i(Q, pp', z) = \delta_{pp'} G_2^{i,(0)}(Q, p, z) + \frac{1}{\Omega} G_2^{i,(0)}(Q, p, z) \sum_q V_C(q) G_2^i(Q, p + q, p', z),
\]  

(2.12)

which corresponds to summing the ladder diagrams, as for the \( T \)-matrix approximation used by Bronold and Fehske [31]. For \( i = 1 \) the non-interacting form is given by the product of the corresponding one-electron Green functions:

\[
G_2^{1,(0)}(Q, p, t - t') = G_e(P_e(p, Q), t' - t) \cdot G_1^e(P_e(p, Q), t - t').
\]  

(2.13)

For \( i = 2, 3 \) the same replacements as for \( G_2^i \) have to be performed.

2.3. Phonon self-energy

Using the electron–phonon interaction (2.7) the usual many-body procedure leads to the self-energy for a given phonon mode \( \alpha \). We focus on the contributions that—in a similar way as the one for electrons—show the coupling of the lattice modes to e–h correlations. The weight of the contribution for each mode is determined by the coupling functions \( g_{\alpha e}(p, q\alpha) \). Yoshida and Motizuki [7] estimated the strength of these couplings for \( 1T \)-TiSe\(_2\) and came to the conclusion that the lowest-lying transverse phonon mode, \( \alpha_{1s} \), in the vicinity of the L-points interacts most strongly with e–h excitations. This is the soft mode, the frequency of which is strongly temperature dependent. At L, it goes to zero around 200 K [4, 5], initiating the formation of a
lattice transformation accompanied by a CDW. The displacement mode according to which the atoms are moved in this transformation has the same spatial structure as the polarization vector of this transverse phonon mode at L.

The self-energy of this transverse phonon mode $\alpha_i$ for wave vectors $Q$ in the vicinity of the $L_1$ point is given by the following expression:

$$\sigma_{ph}(Q, z) = i \sum_{pp'} \left( g_{cc}(P_v(p, Q), Q + w_1, \alpha_i) g_{cv}(P_v(p', Q), Q + w_1, \alpha_i) G_2^{i}(Q, pp', -z) + g_{cv}(P_v(p, Q), Q + w_1, \alpha_i) g_{cv}(P_v(p', Q), Q + w_1, \alpha_i) G_2^{i}(Q, pp', z) \right). \quad (2.14)$$

### 3. Calculations

#### 3.1. The $e$–$h$ correlator

We first evaluate $G_2^{i}$, which is the basic quantity entering the expression for various self-energies. The Bethe–Salpeter equation (2.12) can easily be solved for the case of a local potential $V_e(q) = V_0$. One can then integrate out the relative momenta of the particles forming the pair. This leads to a simple equation for the quantity $X_i$ introduced in (2.10):

$$X_i(Q, z_y) = X_i^{(0)}(Q, z_y) - \frac{V_0}{\xi_2} X_i^{(0)}(Q, z_y) X_i(Q, z_y), \quad (3.1)$$

where $X_i^{(0)}$ involves the product of the corresponding one-electron Green functions:

$$X_i^{(0)}(Q, z_y) = \frac{i}{(-i \beta)} \sum_{z_\beta} \sum_p G_v(p, Q, z_\beta - z_y) G_c^{i}(P_v(p, Q), z_\beta). \quad (3.2)$$

The explicit form of $X_i$ is then

$$X_i(Q, z_y) = \frac{X_i^{(0)}(Q, z_y)}{1 + \xi_2 X_i^{(0)}(Q, z_y)}. \quad (3.3)$$

In principle, a self-consistent calculation should be performed for the one-electron Green functions entering (3.2) by using the self-energy expressions (2.9a) and (2.9b). We present here the first-order approximation using the non-interacting band Green functions:

$$X_i^{(0)}(Q, z_o) = \sum_p \frac{N_F(\epsilon_v(P_v(p, Q))) - N_F(\epsilon_{v}^{i}(P_v(p, Q)))}{z_o - (\epsilon_{v}^{i}(P_v(p, Q)) - \epsilon_{v}(P_v(p, Q)))}. \quad (3.4)$$

For the numerical calculation, we use the following values for the parameters of the band dispersions:

$$E_v = 30 \text{ meV}, \quad E_c = -40 \text{ meV}, \quad m_v = m_e, \quad m_{cx} = 5.5 m_e, \quad m_{cy} = 0.5 m_e. \quad (3.5)$$

This corresponds to a semi-metallic compound. Each conduction band Fermi surface ellipse in the $xy$-plane, when backfolded from the corresponding $L_1$ point to the center $\Gamma$ of the Brillouin zone, has four crossing points with the Fermi surface circle of the valence band, as shown in figure 1(a). The combination of Fermi–Dirac functions showing up in equation (3.4) determines the region in momentum space where the interaction between the hole and the electron is attractive (region III in figures 1(a) and (b)), which allows for the formation of virtual fluctuating bound states. It turns out that the hole must be created in an occupied state of the
Figure 1. (a) The model Fermi surface considered in this paper leading to the commensurate superstructure. It consists of a circular (blue) hole pocket, centered at $\Gamma$, and an elliptic (red) electron pocket, centered at $L$ (shifted here to $\Gamma$ for emphasizing the crossings between them). (b) The hole pocket is formed by the valence band and the electron pocket is formed by the conduction band, which give rise to a semi-metallic configuration (dispersions shown for $k_y = 0$). The real (c) and imaginary (d) parts of $X(Q, \omega + i\varepsilon)$ for $Q = 0$ reveal the Thouless instability at 200 K.

valence band, such that its momentum is larger than the Fermi momentum, and the electron is promoted to an unoccupied conduction band state. One could also excite the electron from the filled part of the conduction band to the empty part of the valence band, but then the interaction is repulsive (region I in figures 1(a) and (b)). These facts are known as the ‘Pauli blocking principle’ [31]. Figures 1(a) and (b) show our model band structure and the domain in $k$-space for which fluctuating e–h pairs can favorably be created.

In figures 1(c) and (d), we present the real and imaginary parts of $X(Q, \omega + i\varepsilon)$ for $Q = 0$ and for different temperatures. It turns out that the real part has its maximum at $\omega = 0$, the value of which increases for decreasing temperature. It will diverge when the denominator in equation (3.3) vanishes. This corresponds to the Thouless instability, which is well known in the framework of the $T$-matrix approximation [33]. Contrary to the case of a semi-conducting band structure—with a positive band gap between the bands—these fluctuating e–h states are not real excitons. They are unstable since they lie in the e–h continuum of the semi-metal. This situation is analogous to low-temperature and overdoped high-temperature superconductors, where fluctuating Cooper pairs form above the transition temperature $T_c$, leading to divergence of the $T$-matrix at $T_c$ [33]. Below the temperature $T_c$ at which this instability happens, the system can stabilize itself by forming a condensate of excitonic bound states. We will later comment on the role electron–lattice interaction may play in this context.
Figure 2. Upper part: the real part of $X(Q, \omega + i \epsilon)$ is shown as a function of $Q$ and $\omega$ in a false color plot (middle) with the corresponding curves (right) for a semi-metallic configuration where the hole pocket is crossing the electron pocket at the Fermi energy (left). The instability is then occurring at $Q = 0$. Lower part: the same for a semi-metallic configuration where the hole pocket is smaller than the electron pocket at the Fermi energy so that there are no crossing points (left). The instability is then occurring at $Q \neq 0$. These data have been calculated at $T = 210$ K.

The $Q$-dispersion of e–h correlations (the real part of $X(Q, \omega + i \epsilon)$) is shown in the upper part of figure 2. For all directions of $Q$ the highest value is at $Q = 0$, where it occurs for zero frequency. This shows that the Thouless instability indeed takes place at $Q = 0$ and $\omega = 0$. The explicit form (3.4) of $X^0_i$ shows that, for a given temperature, its largest value is reached for $Q = 0$ and $\omega = 0$, and this is where the divergence in the real part of $X_i(0, \omega + i \epsilon)$ occurs.

This fact has a simple explanation: e–h transitions, profiting from an attractive interaction and taken into account in the expression for $X^0_i$, correspond to the smallest denominator in equation (3.4) when they occur in the vicinity of the crossing points of the Fermi surfaces shown in figure 1(a). In this case the electron and the hole have essentially the same momentum. Thus the center-of-mass momentum of the pair is given by $w_i$, corresponding to $Q = 0$ (see the upper part of figure 2, left). We stress here that the divergence of $X_i$ at finite temperature is not due to a divergence of the $p$-sum in $X^0_i$ (equation (3.4)), but due to the vanishing of the denominator of $X_i$ in equation (3.3). It happens at the temperature at which $\text{Re}[X^0_i(0, 0)]$ reaches the value $-\Omega/V_0$.

In the case of a band structure which would still be semi-metallic but the Fermi surface of the valence band would have a smaller radius and would lie totally inside the backfolded ellipse of the conduction band Fermi surfaces (see the lower part of figure 2), the zero energy e–h excitations would have a non-zero wave vector $Q$, which would have to connect the two
Fermi surfaces. On the other hand, in the case of a semi-conducting structure the most favorable case for creating an e–h pair takes the hole at the maximum of the valence band and promotes it to a minimum of the conduction band, which again corresponds to a singularity occurring for $Q = 0$ (not shown here).

The case of a Fermi surface leading to a Thouless instability at $Q = 0$ is an important fact for the form of the structural transformation that takes place in $1T$-TiSe$_2$, since it allows for a commensurate structural deformation, as is observed in the low-temperature CDW phase. We will come back to this point later in connection with the spectrum of the lowest transverse phonon mode. The use of a local potential allows for a simple insight into the form of e–h correlations for different center-of-mass wave vectors. A more realistic non-local potential, corresponding to a screened Coulomb interaction, should essentially lead to the same result, changing only the details of the structure of $X(q, \omega + i\varepsilon)$.

3.2. Electron self-energies and spectral functions

We again limit the calculation to the lowest order by replacing the one-electron Green functions in the self-energy expressions (2.9a) and (2.9b) by the free electron form. The resulting self-energies $\sigma_v(k, \omega + i\varepsilon)$ and $\sigma_c(k, \omega + i\varepsilon)$ for the valence band, respectively the conduction band, are presented in figure 3 (left and right, respectively). One can see that the maximum value in the imaginary part of $\sigma_v(k = 0, \omega + i\varepsilon)$ lies near the energy value of the conduction band at L, and the imaginary part of $\sigma_c(k = 0, \omega + i\varepsilon)$ is structured near the valence band energy at $\Gamma$. This is a consequence of the form of the self-energy expression, which relates a given band to the other band, and to the fact that $X_i(q, \omega + i\varepsilon)$ has its highest weight for $Q = 0$ and $\omega = 0$. In the case of an excitonic condensate, introduced into the electronic Green function in a mean field approximation [8, 15], the self-energy is a delta function peaked at the energy value corresponding to the dispersion of the other band. This shows that the e–h fluctuations indeed ‘prepare’ the effects of stable e–h pairs forming the condensate.
Figure 4. Photoemission intensity maps calculated in the fluctuation regime above $T_c$ (at 250 K) at $\Gamma$ (a) and at L (b), without considering the Fermi–Dirac cutoff. Graphs (c) and (d) show the corresponding EDCs. Graphs (e) and (f) are the same as (a) and (b), but are symmetrized around the band extremum and cut by a Fermi–Dirac cutoff. (g, h) Photoemission intensity maps measured at 250 K at $\Gamma$ (g) and at L (h), from [15]. Guides to the eyes (dashed curves and triangles) have been added to emphasize the faint backfolded band in the calculation (f) and in the experiment (h).

Figures 4(a) and (b) present the spectral functions of the valence band (at $\Gamma$), $A_v(k, \Omega)$, and of the conduction band at L, $A_c(k, \Omega)$, respectively. These spectral functions have been calculated (at $T = 250$ K) with the self-energies shown in figure 3 and calculated for the band structure leading to the commensurate superstructure (see the Fermi surface in figure 1(a) for example), using a local potential $V_0 = 0.4$ eV Å$^3$ (see also [38]).

At $\Gamma$, the presence of e–h fluctuations opens a gap in the valence band, so that the band is now split in to two parts. The upper part, labeled c in figure 4(a), follows mainly the top of the normal phase valence band and displays a larger spectral weight near its maximum. Most interestingly, it lies above the Fermi energy and is therefore not accessible to photoemission. The lower part of the valence band, labeled v in figure 4(a), lies entirely in the occupied states and shows a reduced spectral weight at its maximum, close to the gap. As seen in the corresponding EDCs of figure 4(c), its width (in energy) increases slightly with increasing the binding energy as a consequence of complicated modifications of the spectral function due to e–h fluctuations. The original conduction band at L is also strongly renormalized by the e–h fluctuations, as shown in figure 4(b). No real gap opens at the Fermi energy, but a splitting of the conduction band is also observed here. Part of the conduction band, labeled c, is repelled above the Fermi energy, following a dispersion similar to the band c at $\Gamma$ (see figure 4(a)). Below the Fermi energy, part of the original conduction band, labeled v, is shifted to higher binding energies and is strongly broadened, as observed in the EDCs of figure 4(d).
Our spectral functions present only the first-order renormalization effect of the e–h interaction, since the e–h correlator and the electronic self-energies are calculated using non-interacting band Green functions. A fully self-consistent calculation would necessitate a rather heavy numerical effort. The result can be estimated by the following arguments: the spectral functions in figure 4, reflecting the effect of e–h fluctuations, resemble the spectral functions calculated previously [8, 15, 21] for the excitonic condensate phase, where the presence of e–h bound states leads to a small gap in the spectrum of the backfolded bands. The ‘pseudo-gap’ in the fluctuation phase reduces the effect of the crossing points of the Fermi surfaces, such that the increase of $X_i(0, 0)$ is slower. Using our first-order renormalized Green functions in a second-order calculation would produce similar spectral functions with a weaker backfolding effect and a smaller pseudo-gap. The spectral functions resulting from a fully self-consistent calculation should therefore have a form lying in between the non-interacting bands and our first-order spectra. The agreement with the ARPES spectra, in particular at the L-point, will even be improved.

3.3. Phonon self-energies and renormalized dispersion

Various authors [3–5, 34] have attributed the softening of the transverse mode to the temperature dependence of the electronic susceptibility that renormalizes the phonon frequencies. It is usually evaluated for independent electron bands. In our self-energy (2.14) the independent electron susceptibility is replaced by the e–h correlator, calculated taking into account the Coulomb interaction by solving the Bethe–Salpeter equation.

Replacing the full electron–phonon coupling function $g_{xc}(k, q, \alpha)$ by a constant $g$, we obtain the following expression for the phonon self-energy:

$$\sigma_{ph}(Q, \omega) = |g|^2[X_1(Q, \omega) + X_1(Q, -\omega)],$$

which again involves the e–h function $X_1(Q, \omega)$ calculated in section 2.

For reasons that will be discussed below, we use a Coulomb parameter $V_0 = 0.375$ eV Å$^3$, which is slightly smaller than the value chosen in sections 3.1 and 3.2 and leads to the Thouless instability at $T_{cs} = 180$ K. A suitable value for the averaged electron–phonon coupling constant $g$ has been calculated from our previous work (see equation (4) in [24]; the values displayed below are in good agreement with those in [25]). We also need a bare phonon frequency $\omega_0$ based exclusively on the lattice forces. We choose a value measured at a temperature sufficiently above the temperature $T_{cs}$ of the CDW transition. In order to show different types of behavior, we present our results for two scenarios:

(i) $g = 0.7 \times 10^{12}$ eV Å$^{-1}$ kg$^{-1/2}$ and $\omega_0 = 2\pi \times 0.85$ THz,

(ii) $g = 1.1 \times 10^{12}$ eV Å$^{-1}$ kg$^{-1/2}$ and $\omega_0 = 2\pi \times 1.3$ THz.

In figure 5(a), we present the frequency dependence of the phonon spectral functions $A(Q = 0, \omega)$ at an L-point for different temperatures for scenarios A and B in the upper and the lower graphs, respectively. An effective phonon frequency $\omega_{eff}$ can be defined as the place where $A$ has its peak. For a given coupling strength and a given $T$ dependence of $X_i(Q = 0, \omega + i\epsilon)$ it decreases with decreasing $T$, until the mode becomes soft at the instability temperature $T_{cs}$, as shown in figure 5(d). In both cases, the peak of $A(Q = 0, \omega)$ corresponding to $\omega_0$ at high...
Figure 5. Scenarios A (above) and B (below) of the phonon renormalization. (a) Phonon spectral functions obtained by the phonon self-energy in equation (3.6). (b) Phonon Green functions related to the cross section for inelastic scattering. (c) Temperature dependence of $F(\omega)$ with the central peak in scenario B. (d) Temperature dependence of the phonon renormalization obtained by the peak positions of the spectral function.

temperature diminishes in amplitude with decreasing $T$ while its width enlarges. At a cross over temperature $T_{cr}$, the width is such that the peak becomes not well defined (before diverging with $T$ approaching $T_{cs}$).

The main difference between the two scenarios can be seen by defining the effective frequency by the zero of the function

$$F(\omega) = \omega^2 - \omega_0^2 - \text{Re}[\sigma_{ph}(\omega)].$$

Figures 5(c) show that in scenario A (upper graph), $F$ has a minimum at $\omega = 0$ and two zeros at $+\omega_{eff}$ and $-\omega_{eff}$, which go to zero when $T_{cs}$ is approached. However, in scenario B (lower graph) the function $F(\omega)$ develops a local maximum at $\omega = 0$ and a third solution $\omega_{eff} = 0$ appears at the temperature $T_{cr}$. This reminds us of the phenomenon of the central peak that has been observed in structural phase transitions in SrTiO$_3$ and a number of other perovskites, such as LaAlO$_3$ and KMnF$_3$ [26–28].

At high temperatures the temperature dependence of spectral function peaks (figure 5(d)) is relatively flat, whereas closer to $T_{cs}$ it is steeper. This behavior is similar to what is shown in figure 1(d) of [5]. In more detail, this $T$ dependence for the two scenarios is different: in the first

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Figure 6. $Q$ dependence (along A–L) of the phonon renormalization computed for scenario B. The right part is a zoom-in of the left part for intermediate temperatures.

case the curve just changes its slope, whereas in the second case the renormalization is more abrupt (a consequence of the central peak in $F$ going to zero).

In figure 5(b), we also show the phonon Green function $G^<(q, \omega) = A(q, \omega)N_B(\omega)$ of this mode at one of the L-points, $N_B(\omega)$ being the Bose–Einstein distribution function. This function is the main ingredient in the cross section for x-ray inelastic scattering from a given mode at wave vector $q$. For high temperatures the spectral function and $G^<$ have a similar structure, except that $A$ is an odd function of $\omega$ whereas $G^<$ is close to an even function. However, below $T_{cs}$, $G^<$ essentially consists, for both the scenarios, of a central peak of increasing height. This is due to the effect of the Bose function. The presence of the third zero of $F$ in scenario B has only a minor effect on $G^<$.

Recent inelastic x-ray scattering data for this mode in 1$T$-TiSe$_2$ are presented for a few temperatures in [5]. They look similar to our $G^<$, but cannot be directly compared with our theoretical curves, since the diffraction data show a rather strong elastic peak centered around $\omega = 0$.

Figure 6 shows the renormalization of the phonon along A–L calculated in scenario B. The $q$ dependence of $\omega_0$ has been chosen according to the value measured in [4] at 250 K. The renormalization affects only wave vectors close to the L-point, a consequence of the $Q$ dependence of $X_1(Q, \omega)$.

Given the fact that the form of the phonon spectral function substantially differs from a harmonic lattice mode, it is not obvious to give a precise value for the instability temperature $T_{cs}$ of the lattice. A reasonable choice seems to be the temperature at which the steeper part of the curve in figure 5 crosses the temperature axis. For the parameters we have used, we find that $T_{cs} = 200$ K, which corresponds to the experimental value of the CDW transition. We already note that this value is higher than the Thouless instability at $T_{cs} = 180$ K. This is due to the fact that the Thouless instability occurs when the real part of $X_1(0, \omega = 0)$ diverges, whereas the effective phonon frequency goes to zero for a finite value of $X_1(0, \omega = 0)$. We will analyze the consequences of this result in section 5.

We briefly discuss here the constant electron–phonon coupling approximation. As shown in [25], the wave vector dependence of $g_{\lambda\lambda'}(k, q\alpha)$ is relatively weak. Thus, using a constant
coupling function should not influence the basic $T$ dependence of the phonon self-energy dramatically: a double sum weighted by the true coupling functions will not change the fact that the relevant values for $Q = 0$ and $\omega = 0$ strongly increase when the temperature is lowered, thus leading to a softening of the phonon mode at $L$. It may simply change the value of $T_{cs}$, which is anyhow only an estimate.

4. Experimental results

In this section, we discuss the calculated electron spectral function in comparison with our photoemission data. As already stated above, a band structure giving rise to four crossing points (see figure 1(a)) is necessary to obtain an instability at $Q = 0$, leading to a commensurate superstructure. This Thouless instability occurs when the function $X(Q, \omega = 0)$ diverges at $T_{cs}$ (see figures 1(c) and (d)). For this particular Fermi surface topology, we have fixed the local potential at $V_0 = 0.4$ eV Å$^3$, which leads to an instability at $T_{cs} = 200$ K. This value can be motivated as follows. From the plasma frequency measured by Li et al [32] on 1$T$-TiSe$_2$, we obtain a screening length (using the Thomas–Fermi theory) $\lambda = 1.2$ Å. This length is about one half of the nearest-neighbor distance and thus justifies the use of a local potential. The value of the local potential, $V_0$, is then obtained by integrating the screened Coulomb potential over a sphere of radius $r_\lambda$, which should be of the order of $\lambda$. Using $r_\lambda = 1.6$ Å, which is slightly larger than $\lambda$, we obtain $V_0 = 0.4$ eV Å$^3$.

To make a better comparison with photoemission data, the calculated photoemission intensity maps of figures 4(a) and (b) have been multiplied by the Fermi–Dirac distribution (and symmetrized around the band extrema). The resulting graphs are shown in figures 4(e) and (f) (see also [38]). As anticipated above, parts of the bands labeled c are mostly invisible to photoemission and only the part labeled v remains. Due to the intensity rescaling in figure 4(f), an interesting tail appears now at the bottom of the broad conduction band, emphasized by the (blue) triangles and the dashed line.

Figures 4(g) and (h) show photoemission intensity maps of 1$T$-TiSe$_2$ measured (at $T = 250$ K) at $\Gamma$ and $L$, respectively [15]. At $\Gamma$, our present calculations (figure 4(e)) show a good agreement with the experimental data. We recall here that our minimal model contains only one valence band at $\Gamma$, although three valence bands are observed in the experiment (in figure 4(g) the dotted line represents the topmost valence band, present in the model, in addition to the other two valence bands, emphasized by continuous lines). A gap opens at the Fermi energy in the measured spectra, while the valence band shifts to higher binding energies. This gap is indeed well reproduced in our calculations, with a rather correct magnitude. Our calculated spectra also exhibit a loss of spectral weight at the top of the valence band (below the Fermi energy, labeled v in figure 4(e)), although such a loss is more pronounced in the experiment (figure 4(g)).

At $L$, the signature of the CDW phase below $T_{cs}$, consisting of an intense backfolded valence band, is clearest [15]. At this position, the measured data (figure 4(h)) show an unusually broad conduction band below the Fermi energy. This is in agreement with our calculations (figure 4(f)), but there it appears at a too high binding energy. Below this broad band, some remaining high intensity (blue triangles and dashed line in figure 4(h)) anticipates the appearance of the backfolded valence band at lower temperature and is, in that sense, a signature of e–h fluctuations above $T_{cs}$. This feature is also present in our calculated spectra (blue triangles and dashed line in figure 4(f)), although it is weaker there. As mentioned in section 2, the chemical potential is set as the zero of energy. Ideally, it should be repositioned.
as a function of temperature due to modifications of the band dispersions and of their spectral weights. One can anticipate that, to compensate for all the new occupied states available at \( L \), despite the loss of spectral weight at \( \Gamma \), the chemical potential in our calculations (figures 4(e) and (f)) should be shifted to higher binding energies, correcting thus partially for the misplaced conduction band.

5. Conclusions and outlook

Starting from a Hamiltonian describing the main valence and conduction bands with a semimetallic structure in 1\( T \)-TiSe\(_2\) and including a relatively weakly screened Coulomb interaction between the bands, as well as electron–phonon coupling, we have calculated the spectral functions of the electrons and of the lowest transverse phonon mode. The key quantity of our calculation is the e–h correlator, evaluated by solving the Bethe–Salpeter equation, corresponding to the sum of ladder diagrams in which the screened Coulomb potential has a local form. We have compared the theoretical results with experimental spectra: for electrons measured by ARPES \([8, 15, 21]\) and for phonons measured by x-ray scattering \([4, 5]\).

The calculated photoemission intensity maps show good agreement with the experimental data measured above the phase transition, at 250 K. In particular, some spectral features, which are a precursor to the CDW phase and thus a signature of the e–h fluctuation regime, are identified, but their spectral weight is too weak in our calculations compared to the experiment. These discrepancies could be attenuated by considering higher-order terms or by including the electronic self-energies produced by the coupling to the lattice. They would have a similar form as \((2.9a)\) and \((2.9b)\), the e–h correlator being replaced by the phonon spectral function \([38]\). As mentioned in section 4, the band position, which is not correct, could probably also be improved by calculating the chemical potential self-consistently.

Furthermore the e–h correlator reproduces the basic features of the phonon softening mode. Compared to x-ray scattering experiments, the effects of electron–phonon interactions are nonetheless too localized in both temperature (near the transition temperature) and wave vector (near \( L \)). In our calculation, the renormalization at \( L \) above 210 K is too weak and only wave vectors close to \( L \) are affected by the self-energy, while in experiments the renormalization emerges already at half the A–L distance. These observations are a direct consequence of the e–h correlator for our parameter values for the local potential \( V_0 \) and for the electron–phonon coupling strength \( g \). A self-consistent evaluation of the e–h correlator, using the renormalized one-electron Green functions, could lead to an extension of the domain of its influence.

The objective of our calculations was to demonstrate the role and effects of the interband coupling at temperatures above a possible e–h or lattice instability. Electron hole correlations are indeed important and get stronger as the temperature decreases. The Thouless instability of the e–h correlator for \( \mathbf{Q} = 0 \) will be reached at some temperature \( T_{c_1} \) which depends on the strength of the screened interaction and the details of the electronic dispersions. The fact that the divergence takes place at \( \mathbf{Q} = 0 \) is not due to a nesting of the Fermi surfaces of the two bands, but to the existence of crossing points. In a totally rigid lattice this instability at \( T_{c_1} \) would then lead to the formation of an excitonic condensate. The equation determining its amplitude has the same form as the gap equation in the BCS description of superconductivity. The temperature at which the exciton condensate amplitude goes to zero as \( T \) increases coincides with the Thouless instability temperature \( T_{c_2} \).

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However, taking into account the coupling between electrons and lattice vibrations changes the scenario completely. Indeed, the transverse phonon mode, which has the strongest coupling, becomes soft at a temperature $T_{cs}$, which is higher than $T_{c_x}$, since the renormalized phonon frequency at the L points vanishes when the maximum of the e–h correlator is still finite! At this temperature the lattice has to get deformed in order to remain stable. The form of the lattice deformation is known through X-ray diffraction experiments [1, 2, 7]. It is a superposition of the polarization vectors of the soft mode at the three L-points. Recent observations [35] even point to a superposition attributing different phases to the three displacement modes [36], which leads to a chiral structure of the CDW phases in 1T-TiSe$_2$.

These results suggest a combined scenario involving both electronic correlations and lattice instability for explaining the CDW phase of 1T-TiSe$_2$, as has already been suggested [20]. In our way of treating the problem, the central actor is the electron–electron interaction leading to the increasing of the strength of e–h correlations at lowering temperatures. Two instabilities are thus prepared: a soft phonon mode and the formation of e–h bound states. We find that, in a semi-metal, lattice instability should occur before exciton condensation.

In a more sophisticated treatment, the electronic spectral functions and the e–h correlator should, of course, be calculated self-consistently. As mentioned in section 3.2, this should not change the general features seen in the first-order spectra of figure 4. The backfolding effect and the band splitting would simply be weaker than in our first-order form, which would actually be closer to the measured spectra. However, a different value of the potential $V_0$ may be needed to find realistic instability temperatures.

Moreover, the electron–phonon interaction also produces an effective electron–electron potential (explaining, for example, low-temperature superconductivity) which has to be built into a generalized Bethe–Salpeter equation. The resulting e–h correlator may then have a different $T$ dependence. However, before it diverges it will again lead to a soft phonon mode.

Another phenomenon may, however, lead to a different scenario: the combined effect of both interactions can lead to a condensate of ‘excitonic polarons’, i.e. bound states of an electron, a hole and a phonon [39]. If the corresponding electron–hole–phonon correlator increases more rapidly than the e–h correlator, it could lead to a Thouless instability before the phonon mode has become completely soft.

Having established the role of e–h correlations in the undeformed high-temperature phase, the properties of the CDW phase, below $T_{cs}$, should now be studied in more detail. In particular, one has to understand the influence of the lattice deformation, which is supposed to happen before a possible exciton condensation, on the e–h correlations.

First, it is interesting to note that the lattice deformation in the low-temperature phase produces, at least to lowest order in the deformation amplitude, the same type of coupling between valence and conduction bands as the presence of an excitonic condensate. Therefore, the spectra found in the CDW phase could simply be interpreted as a result of the lattice transformation, rather than invoking excitons as we have previously done for explaining the ARPES spectra below $T_{cs}$ [8, 15]. It is, nevertheless, surprising how strongly the backfolded band parts appear despite the modest amplitude of the lattice deformation.

One then has to examine the possibility of formation of an excitonic condensate also in the deformed lattice structure. Given that the deformed band structure will show a small gap around the Fermi energy, the lattice deformation produces a cross over from the semi-metallic to a semi-conducting band structure, in a similar way as has been described for an increasing local interband potential in an extended Falicov–Kimball model [29–31, 37]. In
the deformed phase the e–h continuum will then have a gap in which an exciton band can develop [29]. When the lowest energy in this exciton band goes to zero—i.e. to the chemical potential—these bound e–h pairs will condensate. One might therefore expect to identify another critical temperature—lower than $T_{cs}$—which would signal the transition to an exciton condensate state in the deformed lattice.

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