Temperature dependence of the excitonic insulator phase model in $1T-\text{TiSe}_2$

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ARTICLE INFO

ABSTRACT

Recently, detailed calculations of the excitonic insulator phase model adapted to the case of $1T-\text{TiSe}_2$ have been presented. Through the spectral function theoretical photoemission intensity maps can be generated which are in very good agreement with experiment [H. Cercellier, et al., Phys. Rev. Lett. 99 (2007) 146403]. In this model, excitons condensate in a BCS-like manner and give rise to a charge density wave, characterized by an order parameter. Here, we assume an analytical form of the order parameter, allowing to perform temperature dependent calculations. The influence of this order parameter on the electronic spectral function, to be observed in photoemission spectra, is discussed. The resulting chemical potential shift and an estimation of the resistivity are also shown.

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1. Introduction

The transition metal dichalcogenide $1T-\text{TiSe}_2$ is a layered compound exhibiting a commensurate $(2 \times 2 \times 2)$ charge density wave (CDW) at low temperature [1]. In transport measurements, its signature is a strong anomaly in the resistivity, peaking slightly below the transition temperature $T_c = 200\,\text{K}$. The CDW is accompanied by a periodic lattice distortion involving small atomic displacements. At the same time, a zone boundary phonon softens, being a central ingredient to conventional theories of structural transitions [2]. High resolution angle-resolved photoemission spectroscopy (ARPES) measurements brought a deeper insight into the electronic properties of $1T-\text{TiSe}_2$ by clearly revealing the appearance of new backfolded bands, characteristic of a new periodicity in the system [3–5].

The origin of the CDW can hardly be explained by the usual nesting mechanism [6], because there are notably no large parallel Fermi surface portions [7]. Currently, the best candidates are a band Jahn–Teller effect [8] and the excitonic insulator phase. Recently, the latter scenario has been strongly supported by comparison of ARPES data with theoretical photoemission intensity maps [9]. These calculations are based on the excitonic insulator phase model [10,11], which has been adapted to the particular case of $1T-\text{TiSe}_2$ [12]. The excitonic insulator phase may occur in a semimetallic or semiconducting system exhibiting a small (negative respectively positive) gap. Indeed, for a low carrier density, the Coulomb interaction is weakly screened,

allowing therefore bound states of holes and electrons, called excitons, to build up in the system. If the binding energy E_B of such pairs is larger than the gap E_G, the energy to create an exciton becomes negative, so that the ground state of the normal phase becomes unstable with respect to the spontaneous formation of excitons. At low temperature, these excitons may condense into a macroscopic coherent state in a manner similar to Cooper pairs in conventional BCS superconductors. Exciton condensation may lead to the formation of CDW of purely electronic origin (not initiated by a lattice distortion), characterized by an order parameter Δ. To our knowledge, $1T-\text{TiSe}_2$ is the only presently known candidate for a low temperature phase transition to the excitonic insulator state without the influence of any external parameters other than temperature. Indeed, as pressure is increased above 6 kbar on $\text{TmSe}_{0.45}\text{Te}_{0.55}$ (controlling the gap size and thus the energy necessary to create excitons), a transition to an insulating phase happens, whose origin can also be explained with exciton condensation [13]. In this context Bronold and Fehske proposed an effective model for calculating the phase boundary of a pressure-induced excitonic insulator, in the spirit of a crossover from a Bose–Einstein to a BCS condensate [14].

Here, we study the temperature dependence of the excitonic insulator phase. This is achieved by choosing a simple analytical form for its order parameter and inserting it into the results of our previous calculations [12].

2. Results and discussion

The electronic structure of $1T-\text{TiSe}_2$ near the Fermi energy E_F is composed of three Se4p-derived valence bands at the Γ point

(center of Brillouin zone) and three Ti3d-derived conduction bands distributed among the three symmetry equivalent L points (zone boundary). There is a slight overlap of $\sim$70 meV, such that $1T-TiSe_2$ has a semimetallic character. This issue is still controversial among the ARPES community, but a recent infrared study confirmed the semimetallicity [15]. In an ionic picture, Ti $[Ar]3d^2 4s^2$ gives all its valence electrons to the two neighboring Se $[Ar]3d^{10}4s^2 4p^4$, leaving a system with an empty d^0 shell. In our model, we consider only the topmost valence band (the other two do not cross the Fermi energy and play a minor role) and the three conduction bands. The valence band and the three symmetry equivalent conduction bands give rise to a hole pocket at Γ and electron pockets at L (see Fig. 1(a)). Their band dispersions, ε_v for the valence band and ε_c^i ($i = 1, 2, 3$) for the conduction bands, have been approximated by a parabolic form which describes them well near their extrema, in agreement with ARPES experiment [9].

Our Hamiltonian is composed of a one-electron part H_0, containing the one-electron energies, and a Coulomb interaction part W, which represents the electron–hole interaction between the valence and the conduction bands. Below T_c, this interaction

allows electron–hole pairs, i.e. excitons, to form a condensate described by the order parameter Δ. The calculated Green's functions G_v and G_c describing the bandstructure at Γ and L, respectively, have the following forms [12]:

$$G_v(\vec{p}, z) = \frac{1}{\mathscr{D}(\vec{p}, z)} \cdot \prod_i (z - \varepsilon_c^i(\vec{p} + \vec{w}_i)),$$

$$G_c^i(\vec{p}, z) = \frac{1}{\mathscr{D}(\vec{p}, z)}$$
$$\cdot \left((z - \varepsilon_v(\vec{p})) \prod_{j \neq i} (z - \varepsilon_c^j(\vec{p} + \vec{w}_j)) - |\Delta|^2 \sum_{m,j \neq i} |\varepsilon_{ijm}|(z - \varepsilon_c^m(\vec{p} + \vec{w}_j)) \right)$$

(ε_{ijm} is the permutation symbol). The vectors $\vec{w}_i$, called spanning vectors, correspond to the distance between Γ and the L points. The denominator $\mathscr{D}$, common to both Green's functions, is

$$\mathscr{D}(\vec{p}, z) = (z - \varepsilon_v(\vec{p})) \prod_i (z - \varepsilon_c^i(\vec{p} + \vec{w}_i)) - |\Delta|^2 \sum_i \prod_{j \neq i}(z - \varepsilon_c^j(\vec{p} + \vec{w}_j)).$$

The zeroes of this denominator give the renormalized band dispersions, which depend on the order parameter Δ. They are common to Γ and L, i.e. for G_v and G_c, as one expects for a CDW characterized in our case by the spanning vectors $\vec{w}_i$. The spectral function, $A(\vec{p}, \Omega) = -\text{Im}[G(\vec{p}, \Omega + i\delta)]/\pi$, describes the one-electron spectrum, essential for our purposes. It provides us with the spectral weight (SW) carried by the dispersions in the process of photoemission. Figs. 1(b) and (c) present calculated photoemission spectra at Γ and L along the high symmetry direction ΓM and AL (long axis of the electron pockets) for an order parameter $\Delta = 0$ meV (normal phase) and $\Delta = 100$ meV (CDW phase), respectively. The SW of the dispersions is indicated in grayscale. In Fig. 1(c), the bands indicated by the thin dashed lines have a negligibly small SW, so that they do not appear on these grayscale graphs. We immediately see that the similarity of the bands at Γ and L is only approximate. At Γ, as the order parameter increases, the lower part of the valence band v shifts to higher binding energies, while its top c' shifts above E_F, opening thereby a gap. Some SW is then transferred from v to c'. At L, with an increasing order parameter, the conduction band c does not move but looses SW in favor of the backfolded valence band v and the new band c' (which are the same as those appearing at Γ).

In order to introduce temperature effects in the model in a simple way, we now choose a particular form for the order parameter $\Delta(T) = \Delta_0 \cdot \sqrt{1 - (T/T_c)^2}$ where Δ_0 is its value at $T = 0$ K. This function is drawn in Fig. 2(a) for $\Delta_0 = 100$ meV and $T_c = 200$ K. It is similar to a BCS order parameter, displaying a steep decrease at T_c and a saturation for $T \rightarrow 0$ K. Introducing this order parameter into the denominator of $\mathscr{D}$ and calculating its zeros provides us with the curves of Fig. 2(b). They show the temperature dependence of the band positions at Γ and L. Below the transition temperature, the backfolded valence band v and conduction b and c' shift away from their normal phase positions, exhibiting a behavior very similar to the shape of the order parameter. At the same time, the conduction band c and a symmetry equivalent version c'' stay at their initial position. Considering also SWs and broadening the δ-like peaks with a finite width of 30 meV (for presentation purposes), Fig. 2(c) displays over a wide temperature range spectra at L (not equivalent to Γ due to the SWs), where the excitonic effects are the most spectacular. Here, below E_F, one sees that the evolution of the backfolded valence band v is characteristic of the temperature dependence of the order parameter (as the backfolded conduction band c', which is, however, not accessible to photoemission, since the states are unoccupied). These calculated spectra highlight how the real (experimental)
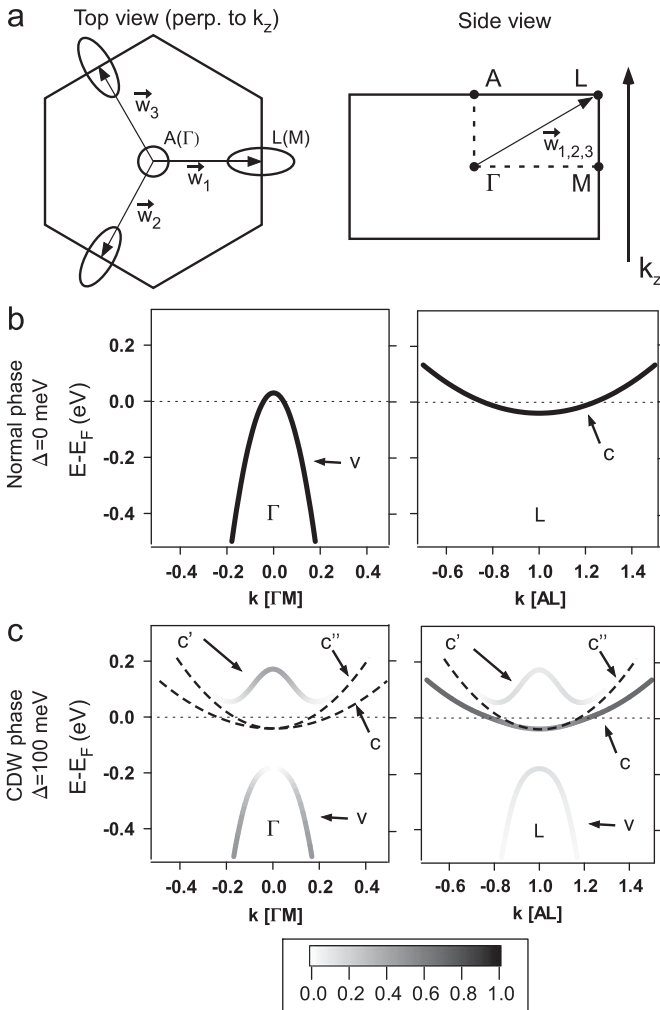

Fig. 1. (a) On the left, schematic picture of the Fermi surface (in the plane perpendicular to k_z) considered in the model, placed on the Brillouin zone of $1T-TiSe_2$. On the right, side view of the Brillouin zone showing high symmetry points. Graphs (b) and (c) show band dispersions with their spectral weight (photoemission spectra) calculated with the spectral function at Γ and L along the high symmetry direction ΓM and AL (long axis of the electron pockets) for an order parameter $\Delta = 0$ and 100 meV, respectively. The spectral weight carried by the band is indicated in grayscale. In graphs (c), the thin dashed lines indicate the position of bands having negligibly small spectral weight.