

CDW phase of $1T$ -TiSe₂: The influence of conduction band population

Matthias M. May,^{1,2,*} Christine Brabetz,¹ Christoph Janowitz,¹ and Ricardo Manzke¹

¹Department of Physics, Humboldt-University of Berlin, D-12489 Berlin, Germany

²Institute for Materials for Photovoltaics, Helmholtz Centre Berlin, D-14109 Berlin, Germany

(Dated: September 9, 2011)

The charge-density wave (CDW) phase of TiSe₂ was studied by angle-resolved photoelectron spectroscopy (ARPES) and resistivity measurements investigating the influence of the band gap size and of a varying population of the conduction band. A gradual suppression of the CDW-induced electronic superstructure is observed for a variation of the band gap in the ternary compounds TiC_xSe_{2-x} with C=(S, Te) as well as for an occupation of only the conduction band by H₂O adsorption-induced band bending. These observations point to an optimum band gap and support an excitonic driving force for the CDW.

PACS numbers: 71.20.Nr, 71.35.Lk, 71.45.Lr, 79.60.-i

Some of the transition-metal dichalcogenides (TMDCs) with their typical quasi-two-dimensional structure were among the first materials where CDW phase transitions have been discovered [1, 2]. TiSe₂, one representative of the TMDCs exhibiting a CDW phase transition, is particularly interesting as the origin of its CDW phase has been under discussion ever since. Amongst others, a Jahn-Teller effect [3, 4], an excitonic origin [5–7] or a mixture of both [8, 9] were proposed, see also [10] for a comprehensive review. A competing superconducting phase was found on Cu intercalation [11] and pressure [12] emphasising the close relationship between the collective charge carrier phenomena CDW and superconductivity. The question whether TiSe₂ is a small-gap semiconductor [8] or a semi-metal [3] has been a long-standing discussion which was answered by Rasch et al. [13] in favour of the semiconductor with a band gap of $E_g \approx 150$ meV. It is generally agreed that the CDW phase transition of TiSe₂ is of second order forming a commensurate $2 \times 2 \times 2$ superstructure below $T_c \approx 200$ K [2]. This results in a reduced Brillouin zone (BZ) as shown in Fig. 1(a). The two most prominent experimentally seizable features of the CDW phase are a peaking resistivity below T_c and the evolution of backfolded bands due to the reduced BZ visible to ARPES. Both signatures will be addressed in this Letter.

The valence band maximum of TiSe₂ derived from Se $4p$ states is found at Γ while the minimum of the conduction band of Ti $3d$ character is located at the BZ boundary at L as schematically shown in Fig. 1(c). In the CDW phase of TiSe₂ both, conduction and valence band shift to higher binding energies and a backfolded valence band appears at L, which represents a new Γ^* point of the CDW superstructure, assigned Γ^* , as depicted schematically in Fig. 1(d). Experimentally determined spectra at the high symmetric points A and L [15] well in the CDW phase ($T=21$ K) are shown in Fig. 2(a) and (b) in good agreement with [6]. At low temperatures, a CDW-induced energy shift Δ is observed and a distinct amount of spectral weight is transferred to the backfolded bands,

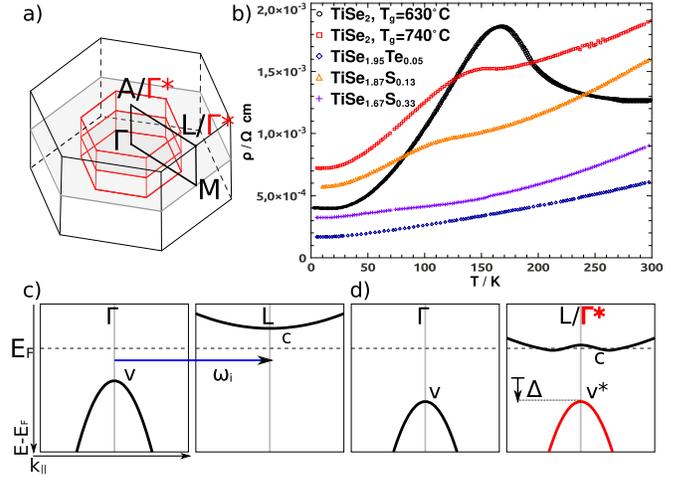


FIG. 1. (Colour online) (a) BZ of TiSe₂ of the normal phase (black) and in the CDW phase (red). High symmetric umklapp points of the reduced BZ are marked by a star. (b) Specific resistivities of different ternary compounds and of pristine TiSe₂ grown at different temperatures. (c) Schematic view of conduction band c and valence band v around their minimum and maximum (with spanning vector $\vec{\omega}_i$) at Γ and L , respectively, in the normal phase (c) and in the CDW phase (d). The backfolded valence band v^* is shown in red with the CDW-induced energy shift Δ . Sketch similar to e.g. [14].

see e.g. Monney et al. [14] for further discussion. In the excitonic model, holes at Γ and electrons at L of Se $4p$ and Ti $3d$ character, resp., form excitons lowering the overall energy of the system. Their different locations in k -space define the spanning vector $\vec{\omega}_i$ giving rise to the electronic superstructure. Therefore, the driving force of CDW formation is of electronic origin, followed by a periodic lattice distortion. In contrast, for a phononic Jahn-Teller like driven CDW, the energy is lowered by a spatial distortion of the crystal lattice. As both models show deficiencies in explaining all experimental observations, a combined model was proposed by van Wezel et al. [9, 16].

In this Letter we present ARPES and resistivity experiments probing the influence of the occupation of the valence and conduction bands on the strength of the CDW phase of the small-gap semiconductor TiSe_2 . At first, the size of the band gap is varied changing the occupation of both, the topmost valence and the lowest conduction band. These results point to an optimal band gap size for a strong CDW, however a decrease of the gap size affects the CDW much stronger than an increase. At second, the occupation of the conduction band is increased by decreasing the occupation of the valence band by an induced bending of these bands. It will be shown that the occupation of the conduction band is the crucial parameter for the CDW evolution.

A variation of the size of the band gap E_g was realised via ternary compounds $\text{TiC}_x\text{Se}_{2-x}$ with C=S and Te. TiS_2 and TiTe_2 are homologous crystallographic and electronic systems to TiSe_2 , but with a different energy gap E_g . TiS_2 is a semiconductor with a positive band gap of about 300 meV [17]. TiTe_2 on the other hand is a semi-metal with a negative band gap of approximately 800 meV [18]. For both, no CDW phase has been reported. As a first approximation, the band gap of ternary compounds $\text{TiC}_x\text{Se}_{2-x}$ can be regarded to change its size linearly with the stoichiometric factor x similar as in other ternary TMDC series [19]. Hence, the ternary $\text{TiC}_x\text{Se}_{2-x}$ series with small x values represent a possibility to study in detail the influence of the band gap size on the CDW formation in TiSe_2 . The single crystals of TiSe_2 and the derived ternary compounds $\text{TiC}_x\text{Se}_{2-x}$ were grown at a temperature $T_g = 740^\circ\text{C}$ by chemical vapour transport using iodine as transport gas. The resistivities in the plane perpendicular to the c -direction were determined using an alternating current of 30 Hz and 20 mA varying the temperature between 2 and 300 K at an alteration rate of 1 K/min. ARPES experiments were performed at the synchrotron source BESSY II (beamline BEST) at a photon energy of $h\nu = 22\text{ eV}$ with an energy resolution of 25 meV and an angle resolution of 0.1° . The samples were cleaved in situ and their temperature was varied between 20 K and 300 K at a temperature stability of $< 1\text{ K}$.

Another way to manipulate the population of the conduction band is rendered possible by the unit cell's structure of TiSe_2 with its van der Waals sandwiches forming natural cleavage planes free of surface states. Karschnick et al. [20] demonstrated the (reversible) enhancement of the Ti $3d$ photoemission by band-bending due to H_2O adsorption. In a simple model, the water molecules of high dipole moment are physisorbed and create a Schottky contact-like bending of the bands [13] and thus allowing a systematic increase of the population of the conduction band at the surface. For the H_2O experiments, water vapour was used in the UHV chamber, its amount specified by the unit Langmuir (L): $1\text{ L} = 1.33 \cdot 10^{-6}\text{ mbar}\cdot\text{s}$. A saturation of the energy shift occurs around 30 kL and

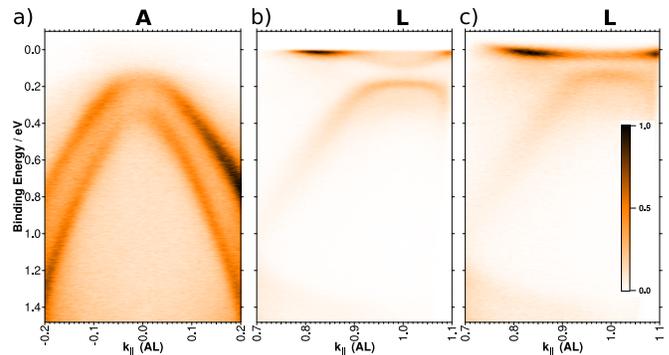


FIG. 2. (Colour online) ARPES intensity maps ($h\nu = 22\text{ eV}$) of pristine TiSe_2 on the AL high symmetry line of the Brillouin Zone. (a) Point A at 21 K (b) L at 21 K (c) L at 140 K.

corresponds to one monolayer of H_2O molecules on the surface and an overall band bending of 130 meV [13]. This technique was also previously used to determine the size of the band gap of TiSe_2 [13]. Although band bending due to water adsorption is a typical surface effect, it should be mentioned that this is exactly the region probed by ARPES. As a purely electronic modification of the population, this would probe the existence of an excitonic driving force.

Results of resistivity measurements are given in Fig. 1(b). For pristine TiSe_2 samples, two different growth temperatures are given. The peak in resistivity is more pronounced at a lower growth temperature ($T_g = 630^\circ\text{C}$) as expected [2], presumably due to less intercalated excess Ti [2, 21]. The experimental signature of a well-developed CDW, the strength of the backfolded bands monitored by ARPES, is however equally strong [22]. Comparing the different stoichiometries for $T_g = 740^\circ\text{C}$, we find a weakening of the resistivity maximum and a shift towards lower temperatures with increasing sulphur content, similar to [2]. For an already very small content of tellurium (stoichiometric factor $x = 0.05$) the maximum disappears completely.

ARPES intensity maps at $L(\Gamma^*)$ are given in Fig. 2 and 3. The gradual suppression of the CDW phase by temperature can be seen comparing pristine TiSe_2 well in the CDW phase at 24 K [Fig. 2(b)] with the spectrum at 140 K [Fig. 2(c)]. For 140 K, the backfolded valence band shifts back towards the Fermi level and becomes less intense. The conduction band also changes with temperature, revealing at 140 K more spectral weight exactly at L. This is due to the fact that the backfolded valence band and the conduction band repel each other deep in the CDW phase, see e.g. [10]. A very similar effect is observed for an adsorption of 3.2 kL H_2O due to a bending of the conduction band in direction to the Fermi energy [Fig. 3(a)], intensity and binding energy of the backfolded valence band decrease and more spectral weight is observed at L. Intensity maps of ternary compounds

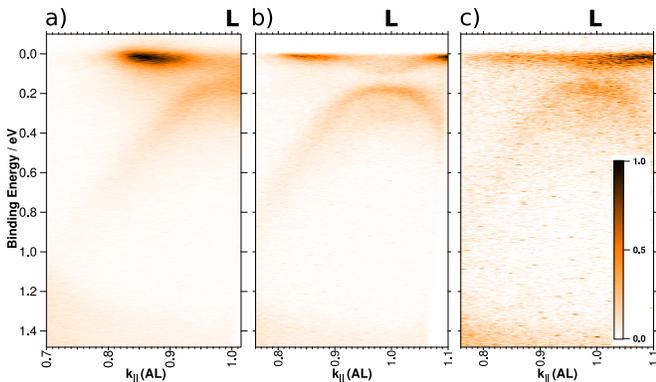


FIG. 3. (Colour online) ARPES intensity maps ($h\nu = 22$ eV) around the high symmetric point L at low temperatures. (a) Pristine TiSe_2 at 22 K, 3.2 kL H_2O (b) $\text{TiS}_{0.13}\text{Se}_{1.87}$ at 31 K (c) $\text{TiTe}_{0.05}\text{Se}_{1.95}$ at 25 K.

$\text{TiC}_x\text{Se}_{2-x}$ in Fig. 3(b) and (c) show a well developed backfolded band for a sulphur content of $x = 0.13$ and a weaker, but still clearly identifiable backfolded Se $4p$ band for a tellurium content $x = 0.05$.

Energy distribution curves (EDCs) of the low-temperature spectra extracted at L are given in Fig. 4. The evolution of the EDCs with increasing adsorption of H_2O is shown Fig. 4(a) revealing a good analogy with the temperature evolution measured by Monney et al. [14]. The two peaks of the backfolded valence band shift towards the Fermi level and loose spectral weight. The second contribution of the Ti $3d$ conduction band, i.e. the prominent peak at ~ 80 meV binding energy in the spectrum at 0 kL [Fig. 4(a)], shifts with more water on the surface similarly towards the Fermi level reducing its intensity. This reveals the gradual suppression of the CDW phase with increasing H_2O -induced conduction band population. These findings are similar to those by Rossnagel [23] who investigated the influence of Rb adsorption.

For the different stoichiometries, EDCs are given in Fig. 4(b), exhibiting an intense backfolded Se $4p$ band for a sulphur content of $x = 0.13$, which evidences an equally well-developed CDW phase as the pristine TiSe_2 . The backfolding is however weaker for both the tellurium sample as well as for the sulphur content $x = 0.33$.

The experimental signatures of the peaking resistivity, measuring a macroscopic property of the bulk, and the ARPES spectra, mapping the microscopic electronic structure, therefore seem to be not strictly correlated. While the resistivity peak quickly decreases for a higher growth temperature and a variation of the stoichiometry, the evolution of an electronic superstructure turns out to be more robust [22], especially to an increase of E_g . Applying the model of a linearly changing band gap with stoichiometry [19], the interpolated value for $\text{TiS}_{0.13}\text{Se}_{1.87}$, showing a well developed CDW phase,

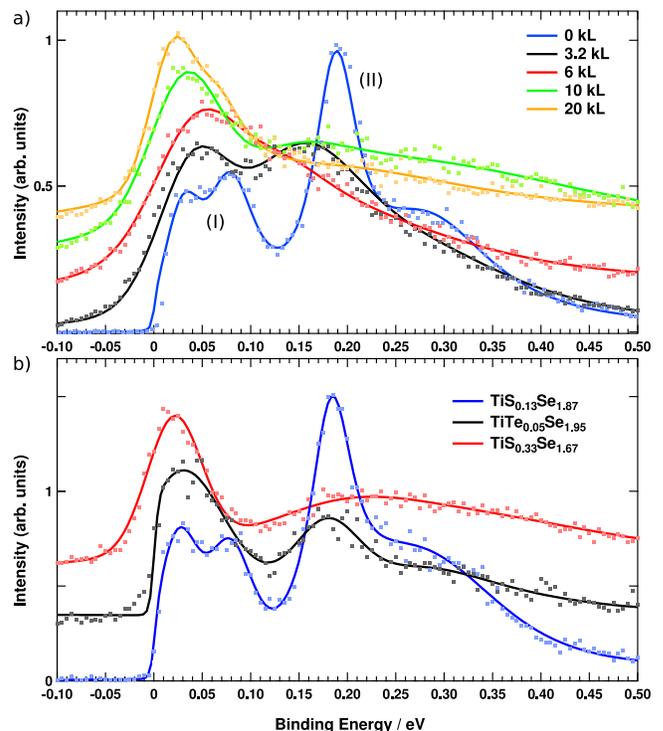


FIG. 4. (Colour online) EDCs extracted at L from the spectra in Fig. 2 and 3. Evolution with increasing H_2O adsorption (a) at low temperatures ($T = 25$ K) and different stoichiometries (b). Solid lines indicate fits, (I) marks the Ti $3d$ derived band, (II) the Se $4p$ derived band.

would be $E_g \approx 170$ meV. A further increase to $E_g \approx 200$ meV for $\text{TiS}_{0.33}\text{Se}_{1.67}$ suppresses the CDW phase as well as a decrease to $E_g \approx 100$ meV for $\text{TiTe}_{0.05}\text{Se}_{1.95}$ indicating the existence of an optimal band gap between 100 and 200 meV. A suppression of the CDW phase by H_2O adsorption can be deduced by the backfolded bands' loss of spectral weight and their shift towards the Fermi level, though the water-induced band bending should shift the bands into the opposite direction. So we find a suppression of the electronic superstructure upon a lowering or a significant increase of the band gap size as well as an additional population of the conduction band. In the following we will discuss which model for the CDW evolution in TiSe_2 fits best to our findings.

Fermi surface nesting has already been regarded as an improbable driving force for the CDW in TiSe_2 due to anisotropic Fermi surface pockets [10]. Our results further emphasise this view as a small variation of the band gap size and conduction band population is unlikely to change the Fermi surface significantly. A Jahn-Teller effect would not only lower the energy of the valence band but also that of the Ti $3d$ conduction band near E_F [4]. Therefore an additional population of the conduction band should not instantly lead to a suppression of the CDW phase. The suppression of the CDW phase by

the (purely electronic) population of only the conduction band due to H₂O-induced band bending however seems to be consistent with the existence of an excitonic driving force. This is similar to the results of Rohwer et al. [7] who deduced an excitonic origin from an ultra-fast response of the CDW phase arguing that the speed of the response could only be achieved by an electronic effect.

Regarding the interpretation of our results within the excitonic model, the asymmetric population of only the conduction band due to band bending provides the key for further understanding of CDW formation in TiSe₂. Obviously the conduction band occupation hinders the formation of excitons. This can be due to (i) a breakdown of the balance between electrons and holes in the conduction and valence band, resp., (ii) an increased screening of the Coulomb interaction between the electrons and holes, (iii) a softening of the well defined spanning vector $\vec{\omega}_i$, or (iv) a combination of several of these effects. For the latter effect (iii) the softening would result from the occupation of the very flat conduction band minimum over a broad regime of \vec{k} values. But in essence it seems to be the self-assembling balance between electrons and holes what stabilises the CDW phase in the small-gap semiconductor TiSe₂ and its robustness against perturbations. Also our finding of an optimum band gap size is a clear hint for such a balance. The weak correlation of the peaking resistivity with the strength of the CDW-induced superstructures accompanied by the umklapp bands measured by ARPES is there again a sign of only weak phononic contributions.

In summary, the stable regime of the CDW phase in TiSe₂ regarding the energy gap and the conduction band population has been probed. While the characteristic hump in the temperature dependent resistivity is very sensitive to small variations of the stoichiometry respectively the size of the energy gap realised by ternary compounds of TiC_xSe_{2-x} (C=S, Te), the transfer of spectral weight into the backfolded bands monitored by ARPES is a much better indicator for the strength and robustness of the CDW phase. The investigated variation of the occupation of the valence and conduction band by both, a symmetric population by changing the band gap size as well as an asymmetric population of only the conduction band minimum by band bending, are in favour of an excitonic insulator instability. This mainly electronic force driving the CDW is however accompanied by a finite electron-phonon coupling causing the periodic lattice distortion in TiSe₂ [10].

The authors would like to thank Stephan Thürmer and Isaak Unger for inspiring discussions and Dr. Helmut Dwelk for his assistance with the resistivity measurements. Part of the work has been conducted at BESSY II. We thank the staff for assistance.

- [1] J. A. Wilson, F. J. Disalvo, and S. Mahajan, *Adv. Phys.* **24**, 117 (1975).
- [2] F. J. Di Salvo, D. E. Moncton, and J. V. Waszczak, *Phys. Rev. B* **14**, 4321 (1976).
- [3] O. Anderson, G. Karschnick, R. Manzke, and M. Skibowski, *Solid State Commun.* **53**, 339 (1985).
- [4] K. Rossnagel, L. Kipp, and M. Skibowski, *Phys. Rev. B* **65**, 235101 (2002).
- [5] T. Pillo, J. Hayoz, H. Berger, F. Levy, L. Schlapbach, and P. Aebi, *Phys. Rev. B* **61**, 16213 (2000).
- [6] H. Cercellier, C. Monney, F. Clerc, C. Battaglia, L. Despont, M. G. Garnier, H. Beck, P. Aebi, L. Patthey, H. Berger, and L. Forro, *Phys. Rev. Lett.* **99**, 146403 (2007).
- [7] T. Rohwer, S. Hellmann, M. Wiesenmayer, C. Sohrt, A. Stange, B. Slomski, A. Carr, Y. Liu, L. M. Avila, M. Kalläne, S. Mathias, L. Kipp, K. Rossnagel, and M. Bauer, *Nature* **471**, 490 (2011).
- [8] T. E. Kidd, T. Miller, M. Y. Chou, and T. C. Chiang, *Phys. Rev. Lett.* **88**, 226402 (2002).
- [9] J. van Wezel, P. Nahai-Williamson, and S. S. Saxena, *Phys. Rev. B* **81**, 165109 (2010).
- [10] K. Rossnagel, *J Phys.: Condens Matter* **23**, 213001 (2011).
- [11] E. Morosan, H. Zandbergen, B. Dennis, J. Bos, Y. Onose, T. Klimczuk, A. Ramirez, N. Ong, and R. Cava, *Nature Phys.* **2**, 544 (2006).
- [12] A. F. Kusmartseva, B. Sipos, H. Berger, L. Forro, and E. Tutis, *Phys. Rev. Lett.* **103**, 236401 (2009).
- [13] J. C. E. Rasch, T. Stemmler, B. Muller, L. Dudy, and R. Manzke, *Phys. Rev. Lett.* **101**, 237602 (2008).
- [14] C. Monney, E. F. Schwier, M. G. Garnier, N. Mariotti, C. Didiot, H. Beck, P. Aebi, H. Cercellier, J. Marcus, C. Battaglia, H. Berger, and A. N. Titov, *Phys. Rev. B* **81**, 155104 (2010).
- [15] Due to the wave vector perpendicular to the crystal surface at $h\nu = 22.0\text{eV}$, the measurement is along the line AL of the BZ. The upper bound of the binding energy difference between the valence band at A and its maximum at Γ is $(40\pm 10)\text{meV}$ [13]. The conclusions of the present paper are not influenced by this small energy difference.
- [16] J. van Wezel, P. Nahai-Williamson, and S. S. Saxena, *Phys. Rev. B* **83**, 024502 (2011).
- [17] C. H. Chen, W. Fabian, F. C. Brown, K. C. Woo, B. Davies, B. DeLong, and A. H. Thompson, *Phys. Rev. B* **21**, 615 (1980).
- [18] R. Claessen, R. O. Anderson, G. H. Gweon, J. W. Allen, W. P. Ellis, C. Janowitz, C. G. Olson, Z. X. Shen, V. Eyert, M. Skibowski, K. Friemelt, E. Bucher, and S. Hufner, *Phys. Rev. B* **54**, 2453 (1996).
- [19] M. Moustafa, T. Zandt, C. Janowitz, and R. Manzke, *Phys. Rev. B* **80**, 035206 (2009).
- [20] G. Karschnick, O. Anderson, W. Drube, and M. Skibowski, *Surf. Sci.* **155**, 46 (1985).
- [21] M. Wiesenmayer, S. Hilgenfeldt, S. Mathias, F. Steeb, T. Rohwer, and M. Bauer, *Phys. Rev. B* **82**, 035422 (2010).
- [22] M. M. May, C. Brabetz, C. Janowitz, and R. Manzke, *J. Electron Spectrosc. Relat. Phenom.* **184**, 180 (2011).
- [23] K. Rossnagel, *New J. Phys.* **12**, 125018 (2010).

* Matthias.May@helmholtz-berlin.de