# Charge-Density-Wave Phase of 1*T*-TiSe$_2$: The Influence of Conduction Band Population

Matthias M. May,[1,2,*] Christine Brabetz,[1] Christoph Janowitz,[1] and Recardo Manzke[1]

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

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

(Received 19 July 2011; published 21 October 2011)

The charge-density-wave phase of TiSe$_2$ was studied by angle-resolved photoelectron spectroscopy 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 charge-density-wave-induced electronic superstructure is observed for a variation of the band gap in the ternary compounds Ti$C_x$Se$_{2-x}$ with $C = (\mathrm{S}, \mathrm{Te})$ as well as for an occupation of only the conduction band by H$_2$O adsorption-induced band bending. These observations point to an optimum band gap and support an excitonic driving force for the charge-density wave.

DOI: 10.1103/PhysRevLett.107.176405 PACS numbers: 71.20.Nr, 71.35.Lk, 71.45.Lr, 79.60.−i

Some of the transition-metal dichalcogenides with their typical quasi-two-dimensional structure were among the first materials where charge-density-wave (CDW) phase transitions have been discovered [1,2]. TiSe$_2$, one representative of the transition-metal dichalcogenides exhibiting a CDW phase transition, is particularly interesting as the origin of its CDW phase has been under discussion ever since. Among 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] emphasizing the close relationship between the collective charge carrier phenomena CDW and superconductivity. The question of whether TiSe$_2$ is a small-gap semiconductor [8] or a semimetal [3] has been a long-standing discussion which was answered by Rasch *et al.* [13] in favor of the semiconductor with a band gap of $E_g \approx 150$ meV. It is generally agreed that the CDW phase transition of TiSe$_2$ 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 angle-resolved photoelectron spectroscopy (ARPES). Both signatures will be addressed in this Letter.

The valence band maximum of TiSe$_2$ derived from Se 4$p$ states is found at Γ, while the minimum of the conduction band of Ti 3$d$ character is located at the BZ boundary at $L$ as schematically shown in Fig. 1(c). In the CDW phase of TiSe$_2$, both the conduction and the valence bands 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 $L$ [14] well in the CDW phase ($T = 21$ K) are shown in Figs. 2(a) and 2(b) in good agreement with Ref. [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; see, e.g., Monney *et al.* [15] for further discussion. In the excitonic model, holes at Γ and electrons at $L$ of Se 4$p$ and Ti 3$d$ character, respectively, 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

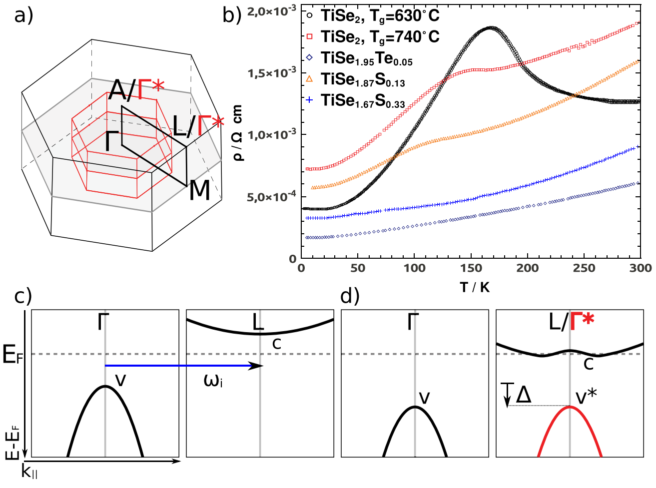

FIG. 1 (color online). (a) BZ of TiSe$_2$ of the normal phase (black) and in the CDW phase (red). High symmetric umklapp points of the reduced BZ are marked by a star. (b) Specific resistivities of different ternary compounds and of pristine TiSe$_2$ grown at different temperatures. (c) Schematic view 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. This sketch is similar to, e.g., [15].

0031-9007/11/107(17)/176405(4)

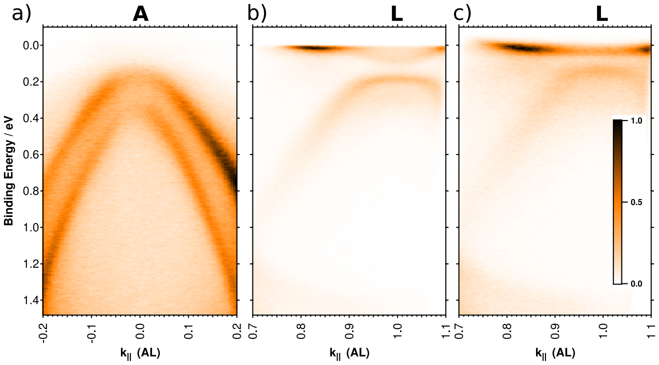

FIG. 2 (color online). ARPES intensity maps ($h\nu = 22$ eV) of pristine $TiSe_2$ on the AL high symmetry line of the Brillouin zone. (a) Point $A$ at 21 K; (b) $L$ at 21 K; (c) $L$ at 140 K.

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 realized via ternary compounds $TiC_xSe_{2-x}$ 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 semimetal 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 $TiC_xSe_{2-x}$ can be regarded to change its size linearly with the stoichiometric factor $x$ similar as in other ternary transition-metal dichalcogenide series [19]. Hence, the ternary $TiC_xSe_{2-x}$ 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 $TiC_xSe_{2-x}$ were grown at a temperature $T_g = 740\,^{\circ}C$ by chemical vapor transport using iodine as the transport gas. The resistivities in the plane perpendicular to the $c$ direction were determined by 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 (beam line BEST) at a photon energy of $h\nu = 22$ 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 and 300 K at a temperature stability of <1 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 3$d$ 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 contactlike bending of the bands [13], thus allowing a systematic increase of the population of the conduction band at the surface. For the $H_2O$ experiments, water vapor was used in the UHV chamber, its amount specified by the unit Langmuir (L): $1\ L = 1.33 \times 10^{-6}$ mbar · s. A saturation of the energy shift occurs around 30 kL and 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 ($T_g = 630\,^{\circ}C$) 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 $T_g = 740\,^{\circ}C$, we find a weakening of the resistivity maximum and a shift towards lower temperatures with increasing sulfur content, similar to Ref. [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 Figs. 2 and 3. The gradual suppression of the CDW phase by temperature can be seen by comparing pristine $TiSe_2$ well in the CDW phase at 24 K [Fig. 2(c)] 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

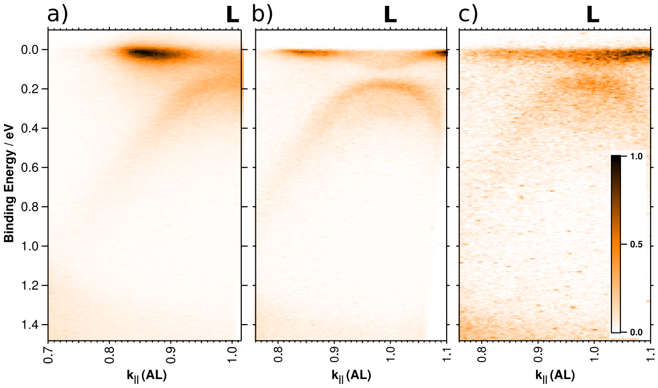

FIG. 3 (color online). ARPES intensity maps ($h\nu = 22$ eV) around the high symmetric point $L$ at low temperatures. (a) Pristine $TiSe_2$ at 22 K, 3.2 kL $H_2O$; (b) $TiS_{0.13}Se_{1.87}$ at 31 K; (c) $TiTe_{0.05}Se_{1.95}$ at 25 K.

observed for an adsorption of 3.2 kL $H_2O$ due to a bending of the conduction band in the 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 $TiC_xSe_{2-x}$ in Figs. 3(b) and 3(c) show a well-developed backfolded band for a sulfur 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.* [15]. The two peaks of the backfolded valence band shift towards the Fermi level and lose 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 sulfur 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 sulfur 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 $E_g$. By applying

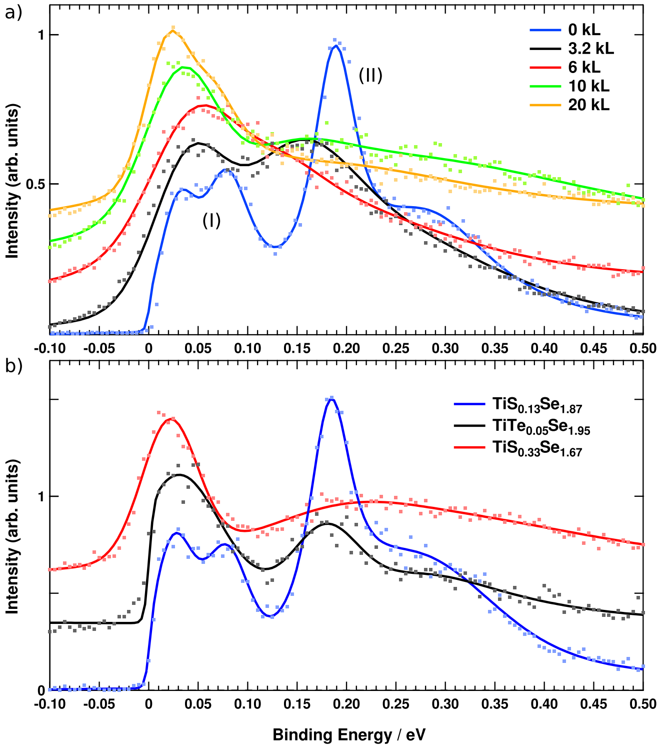

FIG. 4 (color online). EDCs extracted at $L$ from the spectra in Figs. 2 and 3. Evolution with increasing $H_2O$ adsorption (a) at low temperatures ($T = 25$ K) and different stoichiometries (b). Solid lines indicate fits; (I) marks the Ti $3d$ derived band and (II) the Se $4p$ derived band.

the model of a linearly changing band gap with stoichiometry [19], the interpolated value for $TiS_{0.13}Se_{1.87}$, showing a well-developed CDW phase, would be $E_g \approx 170$ meV. A further increase to $E_g \approx 200$ meV for $TiS_{0.33}Se_{1.67}$ suppresses the CDW phase as well as a decrease to $E_g \approx 100$ meV for $TiTe_{0.05}Se_{1.95}$ 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 emphasize 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 lower not only 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 $H_2O$-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 ultrafast response of the CDW phase arguing that the speed of the response could be achieved only 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 $TiSe_2$. 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, respectively, (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 that stabilizes the CDW phase in the small-gap semiconductor $TiSe_2$ 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 $TiSe_2$ 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 and, respectively, the size of the energy gap realized 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 favor 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 $TiSe_2$ [10].

The authors 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.

*Matthias.May@helmholtz-berlin.de

[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**, 16 213 (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. Kallane, S. Mathias, L. Kipp, K. Rossnagel, and M. Bauer, Nature (London) **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] Because of the wave vector perpendicular to the crystal surface at $h = 22.0$ 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 $\Gamma$ is $(40 \pm 10)$ meV [13]. The conclusions of the present Letter are not influenced by this small energy difference.

[15] 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).

[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).