1*T*-TiSe$_2$: Semimetal or Semiconductor?

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Even though the semimetallic behavior of 1*T*-TiSe$_2$ seemed to be well established by band structure calculations and photoemission results, this conclusion has been challenged recently. Two high-resolution photoemission investigations deduced semiconducting behavior, however with a very small band gap. Such conclusion from photoemission is afflicted, in principle, by the problem of determining an *unoccupied* conduction band by photoemission. This problem is solved here by the idea of H_2O adsorption onto the van der Waals–like surface, causing a distinct bending of the bands and resulting in a filled lowest conduction band. The detailed analysis yields undoubtedly semiconducting behavior for 1*T*-TiSe$_2$ and interesting properties of a semiconductor with extremely small band gap.

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Because of the variety of physical properties the layered transition metal dichalcogenides TX_2, with group IVB to VIB transition metals (T) and the chalcogenes S, Se, and Te (X), are the subject of ongoing experimental and theoretical interest [1–3]. The nature of the transition metal dichalcogenides could be metallic or semimetallic, where, e.g., transitions to superconductivity and/or charge-density wave phases become very important [4,5], or semiconducting, where, e.g., the size of the fundamental band gap can be varied almost continuously between zero and values larger than 2 eV [6]. The latter materials are discussed as promising candidates for photovoltaic applications of third generation.

The group IVB transition metal dichalcogenides like TiSe$_2$ crystallize in a layered, quasi-two dimensional structure in which the transition metal is octahedrally coordinated by six chalcogen atoms, the so-called 1*T* structure. Successive Se-Ti-Se sandwich slabs with covalent-ionic bonds are separated by a van der Waals gap, which is the reason for the high anisotropy and the large stability of the [001] surface on the slab. Although there exists a good overall understanding of the electronic structure of these materials, there still remain open questions, e.g., whether the stoichiometric Ti-derived compounds form semimetals or indirect semiconductors at room temperature. TiTe$_2$, for instance, is known to form a semimetal with a small overlap between the Te 5*p*– and Ti 3*d*–derived bands [7,8] of about 600 meV. TiS$_2$, on the other hand, is an indirect semiconductor with a small gap of about 300 meV between the corresponding bands [9–11]. The most challenging compound of this family is TiSe$_2$ with its position between TiTe$_2$ and TiS$_2$. Since selenium is less electronegative than sulfur it is expected that the band gap in TiSe$_2$ is smaller than in TiS$_2$ or even nonexistent. Band structure calculations [12] and former angle-resolved photoemission measurements [10,13–15] came to the result that TiSe$_2$ is a semimetal with a small overlap between the valence band maximum at the Brillouin zone (BZ) center Γ and the conduction band minimum at the BZ boundary L. This result is supported by latest optical spectroscopy experiments [5]. However, recent photoemission measurements [16,17] came to the conclusion that there is a very small band gap between Γ and L. The problem of such an analysis is how to probe an *unoccupied* conduction band and to determine its minimum and the band gap with photoemission spectroscopy.

This problem can be solved by occupying the lowest conduction band of TiSe$_2$ with electrons to make it measurable for photoemission, e.g., under special circumstances by thermal population [18] or by means of physisorption of polar molecules onto the van der Waals-like surface. Indeed, such an effect has been observed for H_2O adsorption on the TiSe$_2$ surface [19]. Especially the Ti 3*d* emission is found to be very sensitive to the exposure to water. If TiSe$_2$ is semiconducting such a change of the occupation of the bands should be due to surface dipole induced band bending, i.e., by accumulation or depletion of the surface layer with carriers and inverting or even degenerating the semiconductor surface.

In this Letter, we report on high-resolution angle-resolved photoemission experiments of stoichiometric TiSe$_2$, taken with He I and synchrotron radiation for different amounts of H_2O adsorbate on the van der Waals-like surface. The results unambiguously identify TiSe$_2$ as a semiconductor with a small indirect band gap.

The TiSe$_2$ single crystals were grown from the elements by iodine vapor phase transport with excess selenium in a temperature gradient of 640–540 °C. The structural quality of the crystals has been controlled by low-energy electron diffraction. Because of extremely weak emission of the Ti 3*d*–type band around the L point of the Brillouin zone it can be deduced that the crystals are very stoichiometric [20,21]. By means of cleaving the samples in ultrahigh vacuum clean surfaces could be readily obtained. The photoemission spectra were taken with He I radiation ($\hbar\omega = 21.22$ eV) produced by a differentially pumped discharge lamp. The electrons were detected using a 180° spherical analyzer mounted on a goniometer which is movable around two independent axes (LEYBOLD-HERAEUS, 3-DARES). Photon energy dependent measurements were performed at the PGM undulator beamline of the Synchrotron Radiation Center (SRC) Madison, Wisconsin in an energy range of $12\ \mathrm{eV} < \hbar\omega < 23\ \mathrm{eV}$. At the synchrotron we used a fixed SCIENTA 2002 analyzer. The Fermi level reference was obtained from a polycrystalline gold film in electrical contact with the sample. The water used as adsorbate was distilled and sterile. The amount of water let into the chamber is specified in langmuirs (L), which is a unit for exposure and corresponds to $1L = 1.33 \times 10^{-6}\ \mathrm{mbar} \cdot \mathrm{s}$. The overall energy and angle resolution applied was 40 meV/1° and 16 meV/0.2° using the LEYBOLD and SCIENTA analyzer, respectively.

Photoemission spectra taken with 21.2 eV photons of the clean $\mathrm{TiSe_2}$ surface and with 160 kL H_2O adsorbate are presented in Fig. 1. Shown are several emission angles ϑ. At this photon energy one measures at a wave vector perpendicular to the surface, $\boldsymbol{k}_\perp$ [22], corresponding to the high symmetric direction AL of the Brillouin zone [13], see Fig. 1. According to Greber *et al.* [18] it is possible to see unoccupied energy bands in photoemission spectroscopy under special circumstances such as narrow band width, flat dispersion, and a sufficiently small energy gap. We find that on the clean sample, a part of the Ti 3d–derived band only appears near the BZ boundary ($M(L)$) for angles around $\vartheta = 30°$, visibly by thermal occupation of empty states within $5k_BT$ of the Fermi level. Hence the condition of a flat band dispersion is fulfilled for the Ti 3d–derived band near the BZ boundary. As ϑ is changed to larger or smaller values, $\vartheta > 40°$ or $\vartheta < 20°$, respectively, the d-band emission disappears completely.

After exposing the sample to 160 kL H_2O one can backtrack the Ti 3d–derived band down to $\Gamma(A)$ as shown in Fig. 2(a). Therefore, at normal emission ($\vartheta = 0°$) three maxima can be found close to the Fermi energy E_F, assigned to the spin-orbit split Se 4p and the Ti 3d emission. This fact suggests a band bending of the bands and a shift of the lowest conduction band below E_F caused by changes of the surface potential due to the weakly bound dipoles. The good detectability of all $\mathrm{TiSe_2}$ photoemission structures at high exposures leads to the assumption that the water is only physisorbed on the surface, i.e., the adsorbate adheres to the surface only through weak van der Waals-like interactions. The effect of enhanced Ti 3d emission after H_2O exposure was already observed by Karschnick *et al.* [19]. They found that only molecules carrying an electrical dipole moment like H_2O and CO lead to an enhancement of the d emission. As shown in Fig. 1, beyond the enhancement the d band becomes visible through the entire Brillouin zone. Exposing $\mathrm{TiSe_2}$ to nonpolar adsorbates like O_2 or N_2 did not show any effect.

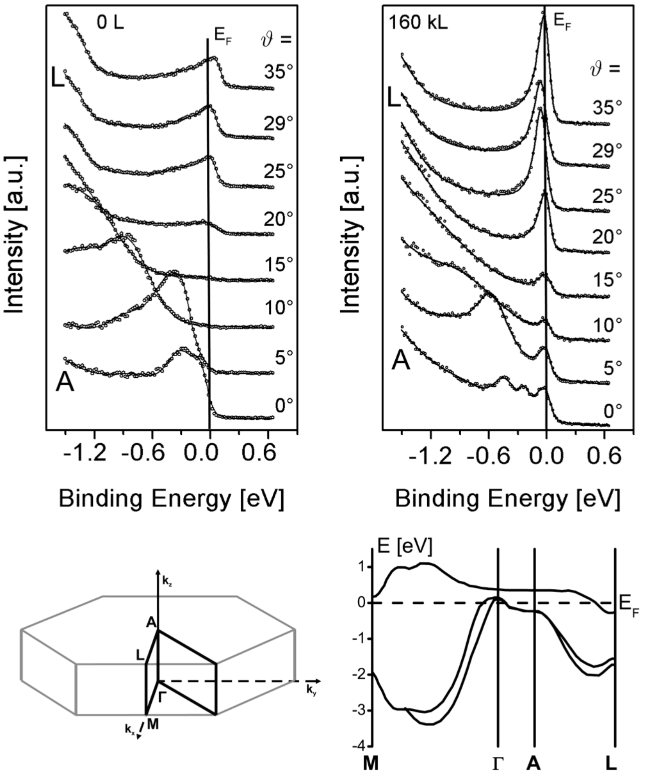

FIG. 1. Top: Photoemission spectra of $\mathrm{TiSe_2}$ taken for different emission angles ϑ along the $\Gamma(A)M(L)$ direction of the Brillouin zone ($\hbar\omega = 21.2$ eV) of the clean surface (left) and after an H_2O adsorption of 160 kL (right). Bottom left: BZ of $\mathrm{TiSe_2}$. Bottom right: Electronic band structure of $\mathrm{TiSe_2}$ (after Zunger and Freeman [12]). Shown are only the Ti 3d–derived band (lowest conduction band) and the Se 4p–derived bands (highest valence bands) at the Fermi energy. Note that [12] obtained semimetallic behavior for $\mathrm{TiSe_2}$ in contrast to the present work. But generally for the Ti dichalcogenides the minimum energy of the Ti 3d bands is at the L point and the maximum energy of the Se 4p bands at Γ.

The evolution of the electronic structure of $\mathrm{TiSe_2}$ as a function of exposure is shown in Fig. 2 for 0 to 160 kL H_2O. According to the photon energy of 21.22 eV one measures for $\vartheta = 0°$ and $\vartheta = 29°$ the A and L points of the BZ, respectively [13]. It is clearly visible in Fig. 2(a) that with increasing amount of water adsorbate the emission maxima shift, and at A a third peak migrates into the spectrum of the spin-orbit split uppermost Se 4p bands, identified as the Ti $3d_{z^2}$ emission. Figure 2(b) shows at the BZ boundary the enhanced intensity of the Ti 3d peak for higher exposures. The saturationlike behavior of the energy shifts as a function of exposure becomes obvious in Fig. 2(c) where the emission maxima resulting from a fit of the experimental curves are shown. The energy shifts of the three bands near E_F are the same, resulting in a band bending of $eV_{\mathrm{bend}} = 130 \pm 20$ meV to lower binding energies. Thus, the lowest conduction band is completely filled and shifted below the Fermi energy for exposures

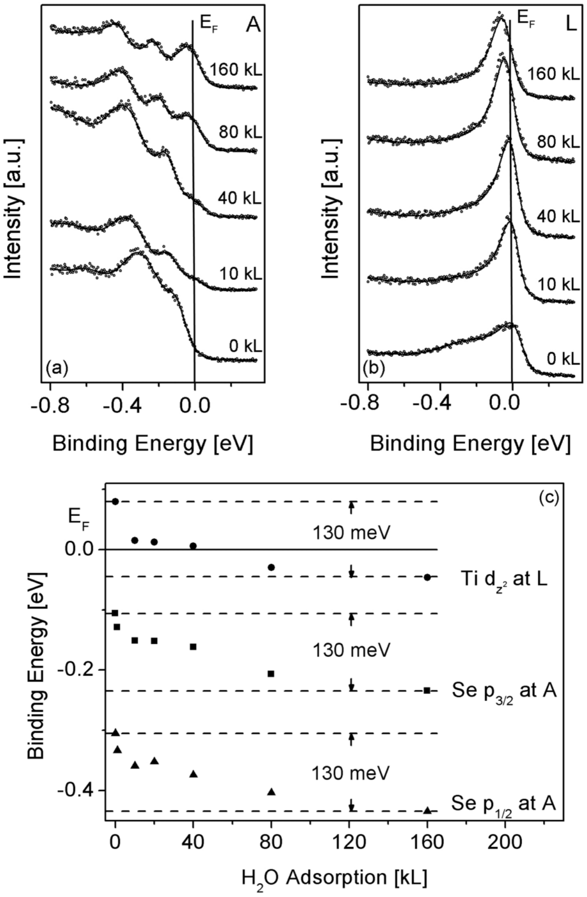

FIG. 2. Photoemission spectra series of $TiSe_2$ as a function of H_2O adsorption. (a) Shift of the uppermost Se $4p$–derived valence bands at an emission angle of $\vartheta = 0°$. (b) Shift of the lowest Ti $3d$–derived conduction band at an emission angle of $\vartheta = 29°$. (c) Emission maxima as a function of H_2O adsorption. $\hbar\omega = 21.2$ eV, room temperature.

of more than 80 kL H_2O [see Fig. 2(c)]. When saturation is reached probably one monolayer of water molecules is adsorbed on the $TiSe_2$ surface. This would result in a sticking coefficient at room temperature of 10^{-4} to 10^{-5}, in agreement with the observations of [19].

Because of the energy shift and the occupation of the lowest conduction band it is now possible to measure the p-d band gap of $TiSe_2$ directly by means of photoemission spectroscopy. In Fig. 3 the spectra measured at the A and the L points of the Brillouin zone are displayed after an exposure to 160 kL H_2O. Because of the fit the center of the Ti $3d_{z^2}$–derived band at L is found to be located at $E_B = -0.05 \pm 0.01$ eV. The Se $4p_{3/2}$–derived band at A has its center at $E_B = -0.24 \pm 0.01$ eV. Hence this points to an indirect band gap between the uppermost valence band at A and the lowest conduction band at L of $E_{\mathrm{gap,AL}} = 190 \pm 20$ meV. This gap is already in contradiction with the calculated band structure of Zunger and Freeman [12] who derived semimetallic behavior, see Fig. 1.

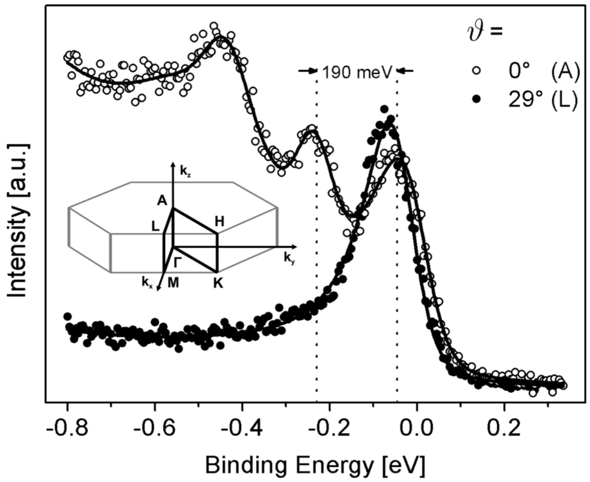

FIG. 3. Photoemission spectra of $TiSe_2$ taken exactly at A and L of the BZ after 160 kL H_2O exposure showing the gap between the lowest Ti $3d$ conduction band at L and the uppermost Se $4p$ valence band at A.

To determine the size of the fundamental band gap E_{gap} of $TiSe_2$, which is the gap between Γ and L (Fig. 1) the dispersion of the Se $4p$–derived bands perpendicular to the surface between A and Γ attains importance. Anderson *et al.* [13] were the first who pointed to the role of dispersion effects in the direction perpendicular to the planes. Because of the incident photon energy of $\hbar\omega = 21.22$ eV (He discharge lamp) the measurements taken in normal emission ($\vartheta = 0°$) are situated near A and not at Γ where the valence band maximum is located. In order to account for the $\boldsymbol{k}_\perp$ effects a tunable incident radiation source is necessary. These experiments were carried out with high resolution at the SRC on the clean sample surface and after water adsorption for photon energies between $12 \text{ eV} < \hbar\omega < 23$ eV. It is found that the $\boldsymbol{k}_\perp$ effects for $TiSe_2$ are very weak with a maximum upper bound for the dispersion of the Se $4p_{3/2}$–derived valence band between Γ and A of 40 ± 10 meV. This result is in some contrast to Anderson *et al.* [13] who derived an upper bound of the dispersion of about 80 meV. Incorporating the $\boldsymbol{k}_\perp$ result, the minimum fundamental band gap between the uppermost p valence band at Γ and the lowest d conduction band at L amounts to $E_{\mathrm{gap,min}} = 150 \pm 20$ meV at room temperature, i.e., $TiSe_2$ is unambiguously identified as a small-gap semiconductor.

In Fig. 4 the schematic band diagram of $TiSe_2$ after H_2O adsorption of 160 kL as deduced from the present experiments is depicted. The experimentally determined values of the band bending of $eV_{\mathrm{bend}} = 130 \pm 20$ meV to lower binding energies and the spin-orbit splitting $E_{\mathrm{s.o.}} = 200 \pm 20$ meV between the upper and lower Se $4p$–derived uppermost valence bands as well as the minimum fundamental energy gap size $E_{\mathrm{gap,min}} = 150 \pm 20$ meV are illustrated as function of the crystal c axis. Note that for the bulk E_F is located almost in the middle of the band gap.

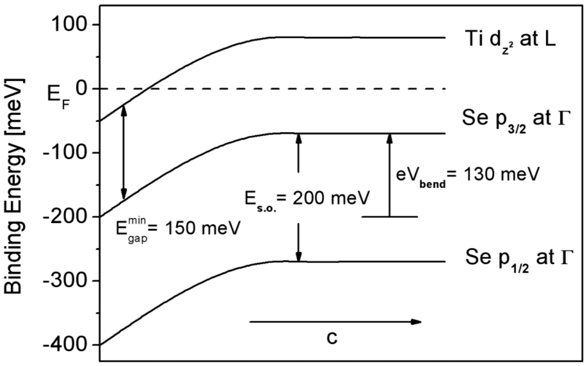

FIG. 4. Schematic band model of $TiSe_2$ after H_2O adsorption of 160 kL. For details see text.

This points to an almost intrinsic semiconductor, in line with the observed weak occupation of the Ti $3d_{z^2}$–derived band for clean samples. The small shift of E_F towards the valence band could either be due to weak accessorily p doping by excess Se atoms in the van der Waals gaps or could also be explained by the ratio of the effective masses of carriers in the valence and conduction band, in agreement with the band structure [9]. Both cases would result in a positive sign of the Hall coefficient R_H, in agreement with the experiment [16].

Because of the van der Waals-like bonding, the $TiSe_2$ surface can be viewed as free of intrinsic surface states, referred to as the Schottky model [23]. Therefore the band bending reflects directly the polarity and density of charges brought onto the surface by adsorption of the polar water molecules. These should stick in such a manner on the surface that the positive end of the dipole causes the Coulomb repulsion to deplete the $TiSe_2$ surface from majoritylike charges. Already low coverages provide an inversion and, according to Fig. 2(c), degeneration is observed for coverages greater than about 40 kL. A detailed quantitative analysis of these challenging properties of a Schottky-like semiconductor with extreme small-gap conditions beyond the Boltzmann approximation will be given elsewhere [24].

In conclusion, it should be mentioned that the observation of band bending due to the adsorption of polar molecules, as discussed above, constitutes by itself unambiguous proof that $TiSe_2$ is a semiconductor. A metallic or semimetallic material would screen the induced surface charge very effectively, preventing the band bending observed here. This has been actually found for the homological semimetallic compound $TiTe_2$ where an exposure to 150 kL H_2O did not induce any band bending [24]. Therefore $TiSe_2$ is unambiguously identified to be a semiconductor. In addition, this result may also help to solve the long-standing question about the origin of the $(2 \times 2 \times 2)$ charge-density wave of $TiSe_2$ at low temperature. With respect to the electrical properties at room temperature there are two groups of models currently discussed; one starts with semimetallic and the other with semiconducting behavior. Consequently, due to the present results only models which are based upon semiconducting behavior can be considered, like, e.g., the excitonic insulator model [15,17,25].

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