Three-Dimensional and Relativistic Effects in Layered 1*T*-TiSe$_2$

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The importance of three-dimensional effects in the electronic structure of the quasi two-dimensional layered crystal 1*T*-TiSe$_2$ is demonstrated by means of high-resolution angle-resolved photoemission excited by synchrotron radiation. By resolving the spin-orbit splitting of the upper Se-4*p* valence band in ΓA we found strong evidence for hole states at Γ. The overlap (<120 meV) between these states and the Ti-3*d* states measured exactly at Γ and L, respectively, is much smaller than previously suggested and is discussed in relation to the structural phase transition below $T_c \simeq 200$ K.

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Layered transition-metal dichalcogenides in the 1*T*-polytype as well as their intercalates exhibit interesting physical properties[1] concerning conductivity, Hall effect, specific heat, and their temperature dependence. Because of their atomic components one finds metallic, semimetallic, or semiconducting behavior, and transitions between these types as well as structural phase transitions in special temperature regions.[1,2]

Although recent experimental and theoretical studies on crystal and electronic structure reveal a good overall understanding of these materials, there remains the long-standing question of whether the stoichiometric Ti-derived compounds form semimetals or indirect semiconductors at room temperature: TiTe$_2$ was shown to form a semimetal with an overlap of about 0.6 eV between the top of the valence *p* bands at the Brillouin zone (BZ) center and the *d* conduction band minimum at the BZ boundary.[3] For TiS$_2$ the most accepted view now is that it is an extrinsic semiconductor[4,5] with an indirect gap of a few tenths of an electronvolt. Its metallic behavior observed in transport properties can be explained by excess Ti.

The most important experimental and theoretical challenge 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 or even vanishes, tending to semimetallic behavior. This is supported by a positive Hall coefficient and thermopower,[6] the pressure dependence of the Hall coefficient,[4] and trends in the optical spectra.[7] On the other hand, band-structure calculations give different results as regards the gap and the values for the overlap,[8-11] and relativistic corrections, in particular the spin-orbit splitting in the vicinity of the Fermi level (E_F), are expected to play a significant role in materials containing Se.[11]

The theoretical results concerning the band structure can be directly tested by high-resolution angle-resolved photoemission spectroscopy (ARPES). Previous ARPES works[12-14] indicate values for the band overlap that vary between 0.18 and 0.5 eV, but no direct evidence for *p*-like hole states at Γ. First, it has to be noted that in these investigations, with the photon energies used, the Γ and the L points in the BZ have not been investigated together which is absolutely necessary to understand the delicate overlap. This means that three-dimensional ($k_\perp$) effects have not been properly taken into account. For the empty *d* states above E_F the existence of such interlayer interaction has recently been shown with use of inverse-photoemission techniques.[15] Second, in all of these investigations the energy resolution was quite poor ($\gtrsim 200$ meV), which makes a distinct conclusion questionable especially for the complicated case of TiSe$_2$. The importance of high energy resolution has recently been demonstrated for the low-temperature charge-density-wave phase of TiSe$_2$.[16] In a recent photoemission study[17] a semiconducting gap was derived from the experimental results which contradicts our findings especially concerning the *p* and *d* band behavior near E_F. Apparently these data were not taken with the resolution claimed so that the very important spin-orbit splitting of the upper Se-4*p* valence band was not resolved, and the data were taken at electron-emission angles which made a correct localization of the Γ and A points impossible.

In this Letter, we report on the first three-dimensional ($k_\perp$) analysis of the electronic valence-band structure of TiSe$_2$ in the ΓA direction down to 6 eV below E_F using ARPES with high energy and momentum resolution combined with synchrotron radiation. A number of important results are obtained: Interlayer interaction is essential for the Se-based valence bands. For a p_z-type Se band we find a strong dispersion up to 1.8 eV along the ΓA direction. The weak but measurable dispersion of the upper spin-orbit–split *p*-valence band causes the band to cross through the Fermi energy near Γ. This proves the existence of holes at Γ.

The preparation and characterization of the TiSe$_2$ single crystals with the best obtainable stoichiometry is described in detail elsewhere.[16] The photoemission spectra were taken with synchrotron radiation from the DORIS II storage ring at HASYLAB in Hamburg in the region 8 eV $<\hbar\omega<$ 30 eV. The monochromator and beam line are described elsewhere.[18,19] The electrons were detected by use of a 180° spherical analyzer mounted on a two-axis goniometer. The measurements were performed with an overall energy resolution of 70 meV $<\Delta E<$ 100 meV and an angular resolution of ±0.5°.

Photon-energy–dependent photoemission spectra were taken in normal emission ($k_{\parallel}=0\pm0.01$ Å^{-1}), providing information along the ΓA direction of the BZ perpendicular to the layers and along ML at the BZ boundary. The resulting band structure for ΓA is shown in Fig. 1. The bands are attributed to Se-$4p$–derived bonding states. Three of them, at binding energies of about 0.1, 3, and 5 eV, show only a small dispersion, whereas one band strongly disperses between 0.35 and 2.15 eV. The latter state obviously has significant three-dimensional character. The value for $k_\perp$ was calculated under the assumption of direct **k**-conserving transitions and of free-electron-like final states. By assigning the minimum and maximum in the binding energy of the strong dispersive band ($\Gamma_2^- A_2^-$) to Γ ($\lambda=950$ Å) and A ($\lambda=565$ Å), respectively, in accordance with all band-structure calculations,[8–11] we derive an inner potential of $V_0=10$ eV. This value is consistent with that used in the analysis of inverse-photoemission[15] and LEED data.[20] The two bands in Fig. 1 at about 0.1 eV (its spin-orbit splitting is not drawn and will be discussed later) and around 3 eV which show only weak dispersion can be attributed to the $\Gamma_3^- A_3^-$ and $\Gamma_3^+ A_3^+$ bands, respectively. The points between 4 and 5 eV correspond to the $\Gamma_1^+ A_1^+$ band. It is split into two components which can be explained by a coupling with two final states with small damping as suggested by LEED-type photoemission calculations.[20] The points at 1 eV around A and 1.5 eV around Γ associated with weak structures in the spectra are not explainable in a direct-transition model and have no counterpart in the calculations. Since they not sensitive to adsorbates they canot be attributed to surface states.[21]

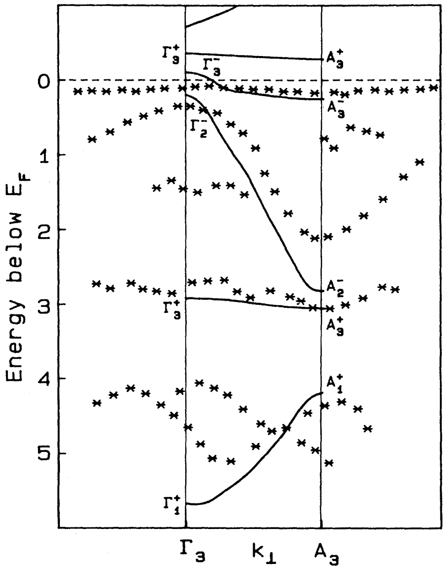

FIG. 1. Comparison between the experimental (asterisks) and calculated band structure (solid lines) (Ref. 9) for the ΓA direction. $k_\perp$ was calculated with use of an inner potential of 10 eV.

The comparison of the experimental results concerning the number of p bands, their binding energies, and dispersions with band-structure calculations[8–11] yields the best overall agreement with the local-density results of Zunger and Freeman[9] (see Fig. 1). However, important differences are obvious. In particular, at A the strongly dispersing p_z-type band is calculated to lie about 1 eV higher in binding energy, yielding a much larger theoretical dispersion. Thus the interlayer interaction is overestimated in this calculation. Likewise, the dispersion of the uppermost p band ($\Gamma_3^- A_3^-$) is somewhat smaller than calculated. For this band we found a weak dispersion of about 80 meV which is of crucial relevance for the electronic character of $TiSe_2$.

In Fig. 2 a series of normal-emission spectra are shown for energies close to E_F as a function of photon energy. The spin-orbit splitting of the uppermost p band in the ΓA direction is observed for the first time. The experimental value of 200 meV is taken from the lower energy distribution curves (EDC's) ($\lambda<720$ Å) and is to be compared to the calculated value of 290 meV.[11] The upper spin-orbit component which appears as a clear peak in the spectra around the A point disappears almost completely around Γ. In addition the slope of the emission cutoff at E_F increases from A to Γ and is finally determined by the Fermi-Dirac distribution at room temperature around Γ. This demonstrates that the upper spin-orbit component crosses the Fermi level between Γ and A, giving the first direct experimental evidence for the existence of hole states at Γ in $TiSe_2$ by photoemission. The spectra given by Chen *et al.*[13] from which the existence of holes around Γ was derived are not consistent with other measurements.[12,14,16] Previous inverse-photoemssion experiments[15,22] did not succeed in detecting the hole states because of limited experimental resolution.

In order to determine the overlap between the occupied uppermost p and the lowest d-derived bands of $TiSe_2$ one has to compare the emission close to E_F exactly at Γ and L as suggested by all band-structure calculations.[8–11] In Fig. 3 the lower spectrum shows the upper p bands at Γ (from Fig. 2) and the upper spectrum shows the emission from the Ti-$3d$–type band at L. In a naive way one would take the maxima of both peaks in the spectra to determine the overlap, which

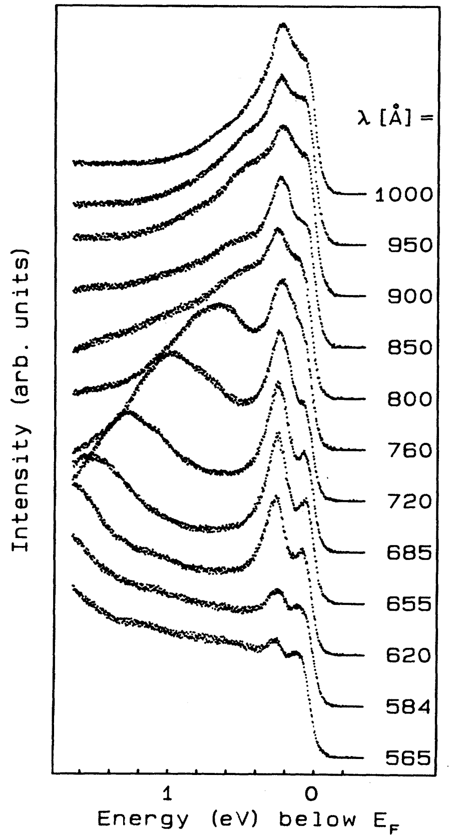

FIG. 2. EDC's taken at normal emission ($\theta = 0° \pm 0.5°$) for the ΓA direction with use of high resolution ($\Delta E = 70$ meV). Spectra are shown for 12 eV $< \hbar\omega <$ 28 eV and scaled with respect to the absolute maxima. The two peaks just below the Fermi level show the spin-orbit splitting of the $\Gamma_3^- A_3^-$ valence band. The strongly dispersive peak belongs to the $\Gamma_2^- A_2^-$ band.

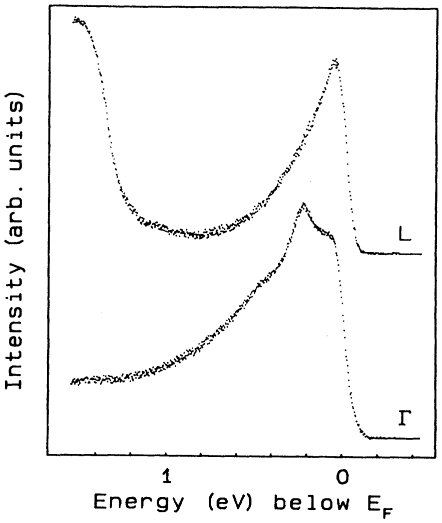

FIG. 3. EDC's taken exactly at Γ and L in the BZ showing the overlap of the Ti-$3d$ band at L and the Se-$4p$ band at Γ.

would yield a value of about 20 meV. However, our high-resolution spectra show that the emission cutoff is clearly determined by the Fermi-Dirac distribution, not seen in the results of Ref. 17. Therefore, a more careful analysis is necessary: (i) From the experimentally determined spin-orbit splitting of 200 meV at A it follows, by addition of this value to the lower spin-orbit component at Γ, that the center of the upper component at Γ coincides with E_F within 10 meV, under the assumption that the splitting is constant along ΓA.[11] Calculations in which the Fermi energy is shifted through a symmetric band profile in order to understand its asymmetric behavior and the experimental observation of the Fermi-Dirac cutoff at Γ (see Fig. 3) indicate that the center of the band could be located slightly (≤ 50 meV) above E_F around Γ. This would be in line with the larger theoretical value for the spin-orbit splitting.[11] (ii) The maximum of the emission associated with the d band at L is located at about 70 meV below E_F. The accurate binding energy of the d band is difficult to determine because of its asymmetric profile.[23] Application of an energy resolution down to 30 meV yields the same profile. Thus the center of the d band can be closer to E_F than the maximum of the d emission shown in Fig. 3, but not more than the half-width of the Fermi-Dirac distribution.

From the upper and lower limits of the p and d band positions given in the above analysis we always obtain a small positive overlap with an upper limit of 120 meV, taking into account the uncertainties of the analysis. A more precise value would require the detailed knowledge of the photoemission profile of a band located very close to E_F, including momentum ($k_\perp$) broadening and other many-electron effects. The overlap of the two bands is very small, contrary to previous ARPES works[12-14] and also to the most recent work[17] where a semiconducting gap is obtained. All of these studies apparently suffered from poor angle and energy resolution.

In conclusion, our results show that in order to understand the peculiar electronic properties of $1T$-$TiSe_2$ it is necessary to perform photoemission studies with high angle and energy resolution using synchrotron radiation combined with high absolute accuracy. Three-dimensional effects are extremely important even for these layered materials. We have observed a critical overlap of p and d states close to E_F, characterizing $TiSe_2$ as a semimetal. Hole states are found for the first time at the Γ point by examination of the $k_\perp$ behavior of the upper spin-orbit split Se-p band which crosses E_F. The investigations show that the center of this band at Γ does not lie more than 50 meV above E_F, indicating that the number of holes is very small.

This explains why previous measurements, including inverse-photoemission studies,[15,22] did not detect these states with the limited resolution applied. The small density of hole states at Γ also favors electron-phonon rather than electron-hole interaction as the driving force for the structural phase transition of $TiSe_2$ below 200 K, in accordance with studies of the electronic structure in the low-temperature phase.[16,24]

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