PHYSICAL REVIEW B VOLUME 31, NUMBER 12 15 JUNE 1985

Interlayer interaction in the conduction bands of layered transition-metal dichalcogenides studied by inverse photoemission

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(Received 19 November 1984)

We have studied the dispersion of the unoccupied Ti $3d$–derived conduction bands in $1T$-TiSe$_2$ along the ΓA direction normal to the basal plane by measuring the photon spectra excited by normal-incidence electrons with kinetic energies between 10 and 20 eV. A triplet structure associated with two low-lying t_{2g}-like d bands and a higher e_g-like d band is clearly resolved within 3 eV above the Fermi level. The t_{2g} bands show noticeable dispersion up to 0.4 eV from point Γ to point A resulting from interlayer interaction. No emission is observed related to empty Se $4p$ states at point Γ near the Fermi level. The results are critically compared with theoretical predictions and optical spectra.

The family of layered transition-metal dichalcogenides (TMDC's) of the type MX_2 (M = group-IVb, -Vb, or VIb metal atom and X = chalcogen atom S, Se, or Te) exhibit very interesting transport, optical, and dynamical properties which vary over a wide range with composition and temperature.[1,2] The layers are built from hexagonally arranged metal atoms, each surrounded by six chalcogen atoms. Between these layers there exists only weak van der Waals interaction so that the crystal's character is essentially two dimensional and large anisotropies in the macroscopic properties are generally observed. Many of these crystals reveal structural phase transitions resulting in superlattices the driving mechanisms of which are discussed using different models.

Three-dimensional effects are often neglected in first-order interpretations of the basic properties of layered materials to simplify the analysis. The interactions normal to the basal plane are, however, very important for the understanding of the full anisotropic properties of these materials. These interactions determine the magnitude of the anisotropy which may vary with the atomic components and structure of the quasi-two-dimensional materials. The full 3D band structure[3–7] turns out to be also critical for the mechanism of phase transitions in certain TMDC's. Interlayer bonding also affects intercalation processes. Apparent discrepancies between the results of different experiments, e.g., photoemission and inverse photoemission, based predominantly on a two-dimensional analysis,[8,9] can probably be resolved by taking into account the full three dimensionality of the crystals.

The starting point for a microscopic understanding of the observed peculiar macroscopic properties of these materials is their electronic band structure, particularly that of the occupied and unoccupied states in the close vicinity of the Fermi level E_F. In this critical energy range the metal d-derived conduction bands are expected to lie within the 5–10-eV-wide bonding-antibonding chalcogen-derived s-p gap. Several band structure calculations based on different theoretical methods have been performed for a number of TMDC's in recent years.[3–7] They gave different results concerning energy positions and band dispersions, including the value for the important p-d gap, which critically affect the interpretation of various macroscopic properties and the nature of the structural phase transitions. The calculated bands showed noticeable dispersion perpendicular to the basal planes where wave functions extending normal to the layers cause interlayer interaction. These calculations can be effectively tested on both sides of E_F by angle-resolved photoemission and inverse photoemission.[8,9] Previous inverse photoemission studies[8,9] have been restricted so far to two-dimensional analysis yielding only the dispersion $E(k_{\parallel})$, for the component of the wave vectors ($k_{\parallel}$) parallel to the surface. They left the perpendicular component $k_{\perp}$ undetermined by reasoning that 3D effects are negligible.

Here we report the first observation of three-dimensional effects in the empty bands of a layered TMDC, a $1T$-TiSe$_2$ single crystal. This was achieved by measurement of the continuous vacuum-UV bremsstrahlung spectrum induced by normal-incidence electrons. $1T$-TiSe$_2$ (space group D_{3d}^3 with octahedral coordination of the Se atoms around the metal atom) has been chosen because it is a prototype material for TMDC's and there already exists a variety of experimental[8,9] and theoretical studies.[5–7] Furthermore, the band structure, particularly that near the Fermi level and its contribution to the phase transition at 200 K, is still controversially discussed. A number of important conclusions can be drawn from our studies. We have observed triple-split d bands in agreement with theoretical predictions. The two low-lying t_{2g}-like bands show significant dispersion up to 0.4 eV in ΓA direction, i.e., normal to the basal plane. This clearly indicates non-negligible interlayer interaction, even for d levels. Despite our good experimental resolution ($\Delta E = 0.3$ eV, $\Delta k = \sim 0.1$ Å^{-1}), we were not able to detect the Se $4p$ hole states at point Γ close to E_F, which have often been discussed as an important feature of the band structure, in connection with the structural phase transition below 200 K, which reveals a $2a_0 \times 2c_0$ superlattice. In addition, our results affect a recent interpretation of optical spectra for this material.[10]

We have measured the inverse photoemission spectra at room temperature by simultaneously detecting the entire photon spectrum between 8 and 22 eV dispersed by a normal incidence grating by means of position sensitive detectors for fixed electron energy.[11] The electrons impinging normal to the crystal surface were supplied by a Pierce gun equipped with a low work function BaO dispenser cathode. Their kinetic energy ranged from 9.75 to 20.25 eV. The overall resolution (electrons and photons) was about 0.3 eV [full width at half maximum (FWHM)] determined by the steepness of the Fermi edge of evaporated gold films. The 1*T*-$TiSe_2$ single crystals of the best obtainable stoichiometry were grown by an iodine chemical transport reaction with Se excess. The crystal quality was checked by temperature-dependent resistivity measurements, which were carried out from room temperature to below the transition temperature around 200 K.

Our inverse photoemission results are displayed in Fig. 1. The spectra show three distinct maxima, a doublet between 0.5 and 1.5 eV and a singlet around 3.1 eV above the Fermi level. These peaks are associated with empty *d* states. The low-lying strong doublet belongs to the t_{2g}-like band which shows a trigonal splitting of ~0.5 eV. The weaker high-lying singlet belongs to the e_g-like band. These three bands correspond to those recently observed in a study of the dispersion of the *d* bands parallel to the surface, where a bandpass detector with fixed photon energy has been applied for monitoring the bremsstrahlung spectrum induced by varying the electron energy.[8] A closer inspection of our data shows that there is a noticeable energy dispersion, seen as peak shifts, as a function of kinetic energy. This demonstrates that the states have three-dimensional character, i.e., dispersion perpendicular to the layers, in addition to that parallel to the layers.

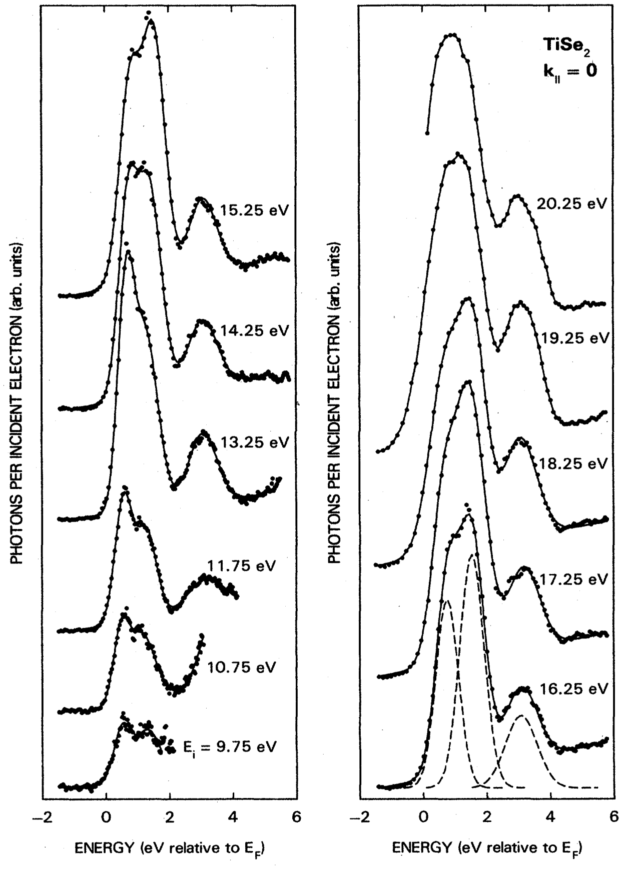

FIG. 1. Normal incidence inverse photoemission spectra of 1*T*-$TiSe_2$ for various initial energies as parameter. The measured spectra are represented by the solid dots, the solid lines show the result of least-squares Gaussian fits, and the dashed lines give an example of the different contributions obtained in that fitting procedure.

A detailed analysis of the data using a least-squares Gaussian fit for the maxima was used to determine the exact peak positions above E_F. The solid lines in Fig. 1 show the result of this fitting procedure and demonstrate the excellent description of the experimental spectra obtained. The associated $k_\perp$ was calculated under the assumption of direct *k*-conserving transitions in the interior of the crystal and parabolic free-electron-like initial states according to the well-known relation

$$k_\perp = \sqrt{2m/\hbar^2}\sqrt{E_{kin}+E_0} \ .$$

In agreement with photoemission and low-energy electron diffraction (LEED) experiments,[9,12] $E_0 = 10$ eV was chosen for the inner potential, i.e., the distance between vacuum level and the bottom of the free-electron parabola. $k_\parallel$, which is conserved during transmission of the electron through the surface, vanishes because of normal electron incidence. The resulting band structure $E(k_\perp)$ is plotted in Fig. 2. The two lowest bands (t_{2g}-character) show a minimum in the center of the Brillouin zone at point Γ with $k_\perp = 2.09$ Å^{-1} and a maximum around point *A* with $k_\perp = 2.62$ Å^{-1} at the boundary of the hexagonal Brillouin zone (both points in **k** space in the third zone of the repeated zone scheme). Between points Γ and *A* the energies are

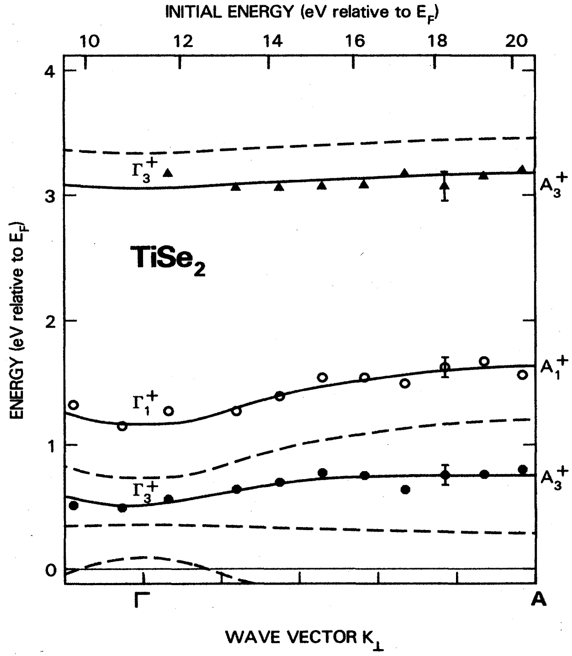

FIG. 2. Experimental dispersion (symbols and solid line) of the unoccupied Ti 3*d* bands in Γ*A* direction normal to the basal plane and comparison with calculated bands (dashed line, Ref. 5).

monotonically increasing. The overall dispersion of the lowest band is ~0.2 eV and of the upper band is ~0.4 eV. No dispersion could be observed within the experimental accuracy for the third band (e_g character).

The number of d bands and their approximate grouping are found to be consistent with band calculations. As a guide, the results of a local-density calculation by Zunger and Freeman[5] are also drawn in Fig. 2 (dashed lines). We attribute the lowest band to that ranging from $\Gamma_{3^+}-A_{3^+}$, the next band to $\Gamma_{1^+}-A_{1^+}$, and the upper band to $\Gamma_{3^+}-A_{3^+}$. There are, however, obvious differences between experiment and this calculation concerning energy positions and dispersions of the bands. In particular, it is noticed that the lowest experimental band shows a monotonic increase of energy from point Γ to point A, while the calculation predicts a decrease. We note here that a tight-binding calculation including nearest-neighbor Se interactions perpendicular to the main layers predicts the observed monotonically increasing behavior between points Γ and A, the second band's dispersion being about twice as large as that of the first.[12] The third band at 3.1 eV should have much smaller dispersion. This is exactly what we observe. We would like to mention here also that there is an interchange of intensity in the low-lying t_{2g} doublet through the Brillouin zone, which has to be related to matrix element effects mainly due to the final states. The observed half-width of the low-lying d bands (0.7–1.0 eV) is due to lifetime effects, the energy resolution being significantly better.

A crucial point of the $TiSe_2$ band structure is the possible Se $4p$–Ti $3d$ band overlap involving the Se $4p$ maximum around the Γ point and the Ti $3d$ minimum at the L point in the Brillouin zone. Such an overlap has been predicted by Zunger and Freeman,[5] but is not found in other calculations, e.g., Ref. 6. Because this feature is relevant to understanding the nature of the phase transition, it deserves special attention. Despite the best spectral resolution we can apply to date in an inverse photoemission experiment, we were not able to detect Se $4p$ hole states at point Γ close to E_F. A strong cross-section effect suppressing the $4p$ emission is most unlikely, as a photoemission study on VSc_2 clearly showed p and d states with comparable intensities.[13] A recent study of $k_\parallel$ dispersion with lower resolution gave the same negative result.[8,9] This result favors electron-phonon interaction as the driving mechanism for the phase transition.

Our results can be compared with recent optical measurements.[10] According to the position of the empty d levels obtained from inverse photoemission, we would expect thresholds for direct optical transitions at approximately 0.5, 1.2, and 3.1 eV, if we assume that the top of the valence band lies just at the Fermi level and we neglect Γ_{3^-}, Γ_{2^-} splitting. Close to the above values distinct steps are observed in the reflection spectra, indicating the onset of absorption due to the three different d bands. The detailed assignment given in Ref. 10, however, is not consistent with our analysis, even allowing for $\Gamma_{3^-}-\Gamma_{2^-}$ splitting and a slight energetic displacement from the Fermi level between 0.2 and 0.5 eV, as suggested by recent photoemission studies, and including the effect of selection rules.

We wish to thank A. Marx and W. Krüger for technical support. M.S. is grateful to IBM Corporation for making possible a fruitful stay at the Watson Research Center, Yorktown Heights, N.Y.

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