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Inverse photoemission study of the conduction bands in $TiSe_2$

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The unoccupied d-like conduction bands of $TiSe_2$ single crystals were studied by momentum-resolved inverse photoemission ($\hbar\omega = 9.8$ eV). The e_g- and t_{2g}-like subbands are identified and found to be nonoverlapping. The dispersion (< 0.3 eV) and the splitting of the d bands is smaller than that predicted by theory, which is due to stronger localization of the Ti $3d$ electrons and possible non-negligible correlation effects.

The large family of layered group-IVb, -Vb, and -VIb transition-metal dichalcogenides (TMDC's) exhibit interesting transport, optical, and dynamical properties which vary significantly with composition and temperature.[1] Due to their two-dimensional character, a strong anisotropic behavior is observed. Many of them undergo phase transitions resulting in superlattices of which the driving mechanisms are discussed using different models. The essential starting point for an understanding of the observed peculiar macroscopic properties of these materials is their electronic band structure, particularly in the vicinity of the Fermi level E_F. In this critical energy range, the metal d-derived conduction bands lie within the large chalcogen bonding-antibonding gap. Several band-structure calculations applying different methods have been made for a number of TMDC's in recent years and yielded different results as regards to energy position and band dispersion.

While the energy dispersion of the occupied bands has been successfully investigated by the powerful method of angle-resolved photoemission (PE), no experimental study of the energy versus momentum relation of the unoccupied states between E_F and the vacuum level was possible. With the development of momentum-resolved inverse photoemission[2-5] (IPE), which has only recently been applied to a few standard metals and semiconductors, one should now be able to study the subtle balance of the electron distribution in this energy range for the TMDC's, and to correlate the results with those from angle resolved PE and thus, finally, with the observed intriguing macroscopic properties. In this new method, uv bremsstrahlung is measured which is stimulated by a well-collimated low-energy electron beam. The electron energy is scanned for different angles of incidence on the target, and thus the electron momentum parallel to the surface is varied, which is considered to be conserved during the interaction process.

Here we present the first momentum-resolved IPE results on a selected TMDC compound: $TiSe_2$. It crystallizes in the trigonal $1T$ structure (space group D_{3d}^3). The aim was to determine the position and dispersion of the unoccupied d bands in this interesting material, with emphasis on the high-symmetry direction ΓM (AL) in the hexagonal Brillouin zone (BZ) where theory predicts a maximum of the chalcogen p bands at the BZ center and a minimum of the lowest metal d band at the BZ boundary.[6,7] The position of the p valence bands, with respect to the d conduction bands around E_F and their possible overlap, which determines whether this material should be considered a semimetal or small-gap indirect semiconductor, have been controversially discussed.[8] In the present experiment, we have succeeded in detecting the important features of the unoccupied Ti d-like bands. Their splitting and dispersion is found to be considerably less than predicted by band calculations. This indicates a stronger localization due either to a smaller overlap of the wave functions or to additional correlation effects not sufficiently taken into account in the available calculations.

In our experiment, we used a new simple photon detection system with a large spatial acceptance angle in connection with a specially built electron gun delivering sufficient current in a well-defined beam down to 1 eV kinetic energy. The momentum resolution is ~ 0.1 Å^{-1}. The electron angle of incidence θ and the azimuthal orientation are varied by rotating the sample. The latter is defined by an *in situ* low-energy electron diffraction study. The bandpass-type photon monochromator uses a CaF_2 window as a low pass and the electron yield of a CuBe multiplier as a high pass. The spectral response of this assembly, measured by synchrotron radiation, yielded a maximum at $\hbar\omega = 9.8$ eV with an energy width of 0.7 eV full width at half maximum (FWHM). Together with the measured energy spread of the electron gun (0.6 eV), the overall energy resolution is 0.9 eV. The observed maximum counting rate was about 10^3 counts/eV sr μA s. Further details of the apparatus are to be published elsewhere.[9] Single crystals of $1T$-$TiSe_2$ with good stoichiometry were grown by an iodine transport reaction and cleaved in ultrahigh vacuum (2×10^{-10} Torr).

The inverse photoemission spectra shown in Fig. 1 reveal two strong emission maxima at 0.5 and 2.6 eV above E_F for normal electron incidence ($\theta = 0°$). They are associated with the unoccupied Ti $3d$ bands. The low-lying peak near E_F is composed of two features which separate as θ increases. The low-energy structure shifts towards E_F with decreasing intensity, whereas the higher-energy component shifts upwards. The observed energy dispersions are < 0.3 eV. The emission at 2.6 eV becomes asymmetric around $\theta = 40°$, but is not resolved into distinct components.

From the peaks in the IPE spectra, we derived the two-dimensional experimental band structure $E(k_{\parallel})$ shown in Fig. 2, using the well-known relation $k_{\parallel} = \hbar^{-1}(2mE_{\text{kin}})^{1/2} \times \sin\theta$ for the momentum component parallel to the surface, i.e., perpendicular to the c axis (E_{kin} is the kinetic energy of the incident electron). In layered compounds like $TiSe_2$, the band electron energy is considered to depend only weakly on the momentum perpendicular to the surface. The experimental $E(k_{\parallel})$ should, therefore, already be a good approximation to the actual band structure which

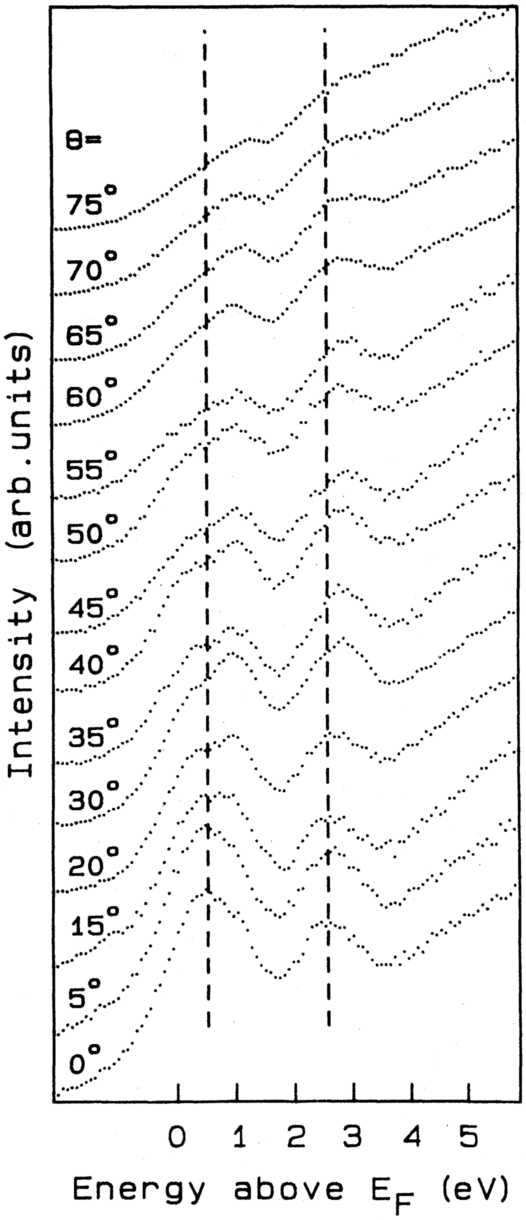

FIG. 1. Inverse photoemission spectra (photon counting rates at $\hbar\omega = 9.8$ eV) for $TiSe_2$ taken in the direction ΓM of the hexagonal Brillouin zone for various angles θ of electron incidence. The dashed lines mark the energy position of the main peaks at normal incidence ($\theta = 0°$).

strongly reflects the two-dimensional character of the crystal. In Fig. 2, we compare our results with the self-consistent local-density linear combination of atomic orbitals calculation of Zunger and Freeman.[6] This theory predicts the conduction bands to be grouped into two nonoverlapping parts, CB1 and CB2. This is also qualitatively understood in a simple ligand field model: In the 1*T* structure, the metal atom is nearly octahedrally coordinated by six chalcogen atoms which splits the Ti 3*d*–derived conduction states into two e_g-like and three lower t_{2g}-like bands. The two strong broad maxima seen in the IPE spectra of Fig. 1

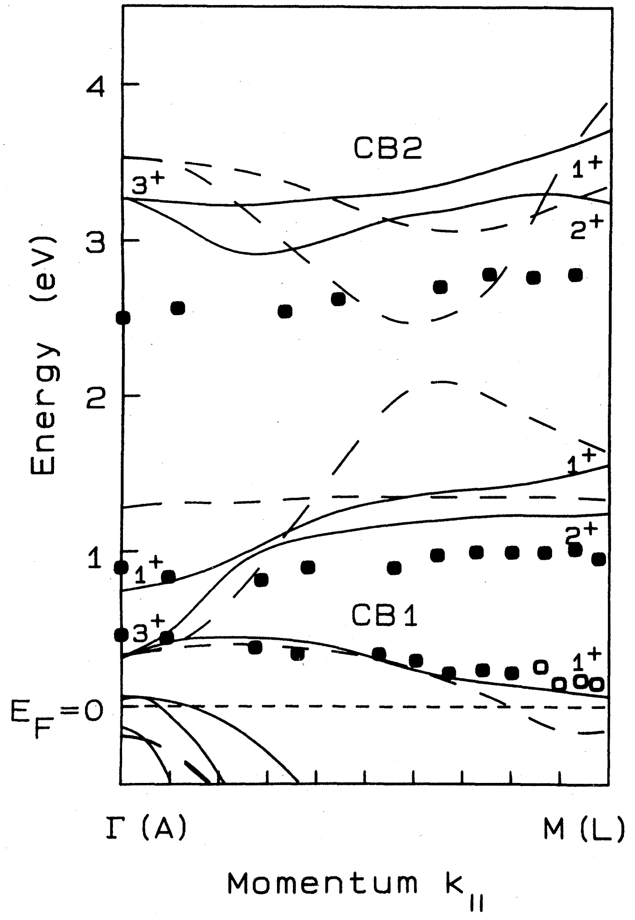

FIG. 2. Comparison of the experimental conduction bands $E(k_\parallel)$ of $TiSe_2$ (symbols) with the calculation of Ref. 6. Solid symbols result from strong features in the inverse photoemission spectra, open symbols corrrespond to weak shoulders. The calculated bands are reproduced for ΓM (solid lines) and AL (broken lines). The symmetry classification belongs to ΓM.

can already be attributed to these two nonoverlapping subbands. It is mentioned that the calculation of Isomäki, Von Boehm, and Krusius,[7] using the self-consistent orthogonal plane-wave method, does not propose a clear grouping in the conduction bands in contrast to our experiment. In agreement with the calculation of Ref. 6 we find additional splitting within the t_{2g}-like bands (CB1), which is derived from the double structured peak near E_F. However, this splitting is significantly smaller than predicted, and the upper subband of CB1 shows less dispersion. Furthermore, the almost dispersionless e_g-like bands (CB2) are found ~ 0.7 eV lower in energy, resulting in a reduced $e_g - t_{2g}$ separation. Due to the localized nature of the transition-metal *d* electrons, which is believed to be strongest in the Ti compounds within group-IV*b* TMDC's,[10] the conduction-band dispersion is already expected to be small. The present experiment indicates that this localization is even stronger than predicted by Ref. 6. In a simple tight-binding model, increasing localization of the Ti 3*d* states would reduce the intralayer overlap between a Ti 3*d* orbital and the next-neighbor Ti 3*d* and Se 4*p* orbitals, thus reducing the t_{2g} splitting in CB1, and simultaneously the $e_g - t_{2g}$ separation consistent with our results. It can also be questioned whether the observed relatively small dispersion can be fully described by a simple band approach. Contributions due to additional correlation effects probably cannot be neglected in order to have a complete understanding of the electronic structure of the *d*-derived conduction bands in these compounds.

The possible indirect overlap between the *d* band minimum at the BZ boundary and the *p* band maximum at Γ has been the subject of controversial discussions both theoretically and experimentally.[6, 8, 11–15] In particular, some models concerning the superlattice formation observed in $TiSe_2$ below 200 K are based on the existence of electron pockets at the BZ boundary and hole states at Γ, which are predicted by the calculation of Zunger and Freeman (see Fig. 2). From IPE we find the dispersion of the lowest *d* band in good agreement with this theory, confirming the location of the conduction-band minimum at the BZ boundary. In addition, the emission due to this band decreases considerably for $k_{\parallel}$ values near the zone boundary, i.e., for $\theta > 50°$, indicating a band crossing through E_F. This is consistent with angle-resolved PE results[12–15] which locate occupied *d* electron states at the BZ boundary. However, we were not able to detect any emission attributable to unoccupied *p*-like hole states at the top of the valence band at Γ. This could be due to the low density of the *p* states or the still limited experimental resolution. On the other hand, an absence of hole states at Γ would also be consistent with recent high-resolution angle-resolved PE measurements,[15] which cannot exclude the existence of a small positive gap in this material, also obtained by a new band calculation.[11] Experimentally, it would be desirable to combine PE and IPE in an *in situ* study to clarify this special point, since it is known that the *d* band results in $TiSe_2$ may depend critically on sample preparation. We also feel that electron-electron interaction during the excitation (deexcitation) process and relaxation effects should not be excluded from discussion to obtain a thorough understanding of the ground state by PE and IPE spectra.

We have demonstrated that by momentum-resolved inverse photoemission one can study the structure of the unoccupied *d* bands in $TiSe_2$ in great detail. We hope that our results stimulate further investigations in the field of inverse photoemission on other TMDC compounds in order to understand the trends of the various macroscopic properties in relation to structure and composition for this interesting class of materials.

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