Photoemission from the (001) surface of 1T-TiSe₂: Comparison of calculation with experiment

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Normal-emission photoemission spectra from the (001) surface of 1T-titanium diselenide have been calculated and compared to experimental energy-distribution curves recorded for various photon energies in the range from 12 to 28 eV. The theory is based on a single-particle one-step model for the emission process. The initial state of the photoelectron is described by means of an empirical tight-binding method, the surface being included via a Green's-function formalism, while a low-energy electron-diffraction scheme is used for the characterization of the final state. Dipole matrix elements are computed numerically. In comparison to the experimental data, the variation of the relative intensities of the photoemission maxima with photon energy, and to some extent these relative intensities themselves, are correctly reproduced by the calculation.

I. INTRODUCTION

Among other transition-metal dichalcogenides the layered crystal 1T-TiSe₂ has gathered great interest, especially with regard to its phase transition at approximately 200 K from the high-temperature 1T phase to the distorted low-temperature charge-density-wave phase.¹⁻⁴ Several theoretical models have been proposed for this transition, their applicability depending sensitively on the electronic band structure in the vicinity of the Fermi energy. Therefore, besides other experimental studies concerning transport properties etc., the electronic structure has been investigated both by angle-resolved photoemission [angle-resolved ultraviolet photoemission spectroscopy (ARUPS) (Refs. 5-9)] and inverse photoemission (bremsstrahlung isochromat spectroscopy¹⁰ and *k*-resolved inverse-photoemission spectroscopy^{11,12}). From our high-resolution photoemission spectra we draw the conclusion that titanium diselenide is a semimetal with a small band overlap < 120 meV.⁸ On the whole, the peak positions in the experimental energy-distribution curves for normal and non-normal emission compare best with the local density self-consistent *ab initio* band structure calculated by Zunger and Freeman.¹³

In the following we shall concentrate solely on the normal-emission case (i.e., ΓA -ARUPS) and photon energies in the range from 12 to 28 eV. Within the direct transition model the bonding energies of the photoemission maxima have successfully been compared with the theoretical ΓA valence-band structure from Zunger and Freeman,¹³ assuming the dispersion of the final state to be given either by a free-electron parabola⁸ or by low-energy electron-diffraction (LEED) Bloch states.¹⁴ The latter

yield an improved correspondence with regard to the experimental data and, moreover, an additional photoemission maximum in the binding-energy range between 4 and 6 eV was traced back to emission from different final-

FIG. 1. Valence-band structure of TiSe₂ in the ΓA direction, taken from Ref. 13.

state Bloch waves, i.e., a so-called umklapp process.

Besides the interpretation of the peak positions we compare experimental ΓA -ARUPS data for 1T-TiSe₂ (Ref. 8) with calculated spectra especially with respect to the relative intensities of the structures in the spectra and the changes in these relative intensities caused by a variation of the photon energy. Our ARUPS theory is based on a single-particle one-step model of the photoemission process, including matrix-element effects and an optical potential. It represents a novel combination of the empirical tight-binding method (ETBM), which is used for the description of the initial state, with a LEED theory for the final state. A glance at the valence-band structure along the ΓA direction in reciprocal space plotted in Fig. 1 reveals a major problem: In distinct contrast to the strongly dispersive $\Gamma_2^- - A_2^-$ band, the $\Gamma_3^\pm - A_3^\pm$ bands are almost nondispersive. Thus, the one-dimensional density of states (DOS) in the energy regime between the two prominent DOS peaks of the $\Gamma_3^\pm - A_3^\pm$ bands is very small. Nevertheless we actually observe large photoemission intensities derived from the dispersive $\Gamma_2^- - A_2^-$ band in the experimental data. Therefore, a quantitative description of the photocurrent necessitates the inclusion of matrix-element effects; one cannot understand the relative intensities on the basis of a weighted density of states alone. This differs, for example, from the situation found by Pollman *et al.*¹⁵ in the case of the GaAs(110) surface for which energy-distribution curves for several angles of incidence are well comparable to a layer average of the density of states. The density of states of the single layers is weighted by the corresponding distance from the surface in order to account for the finite emission depth of the photoelectrons. In this respect titanium diselenide can serve as an interesting test substance for photoemission theories.

After a short description of the crystal structure of TiSe₂ in Sec. II, the ARUPS theory, including some details of the program, will be explained in Sec. III. Thereafter the experiment will be outlined, while the result will be discussed and compared with the calculated curves in Sec. V.

II. THE SUBSTANCE TiSe₂

Titanium diselenide crystallizes in the 1T-CdI₂ structure, the space group being $D_{3d}^3(P\bar{3}m1)$.¹⁶ The unit cell contains one formula unit. The crystal structure is depicted in Fig. 2. The crystal is built up of Se-Ti-Se layers which are stacked on top of each other, only weakly bound over a van der Waals gap. These layers themselves consist of a plane occupied by titanium atoms which is sandwiched by similar planes of selenium atoms on either side. Within each plane the coordination of the atoms is hexagonal with a lattice constant $a = 3.54$ Å. The spacing between the selenium and titanium plane is given in units of the lattice constant $c = 6.00$ Å perpendicular to

FIG. 2. Crystal structure of 1T-TiSe₂. Open circles mark the positions of the selenium atoms and solid circles denote the titanium atoms.

the layers by the parameter $z = 0.255$.¹⁷ However, in the tight-binding calculations the idealized value $z = 0.25$ has been assumed.

On cleaving the crystal along the van der Waals gap a (001) surface can easily be created. The direction normal to the surface coincides with the c axis of the crystal lattice and the ΓA direction in reciprocal space. As we restrict ourselves to normal-emission geometry, the C_{3v} symmetry of the half-space is not destroyed by the boundary condition imposed on the final-state wave function of the photoelectron, which is related to the position of the detector. The small surface relaxation known from LEED investigations¹⁸ is not considered here.

The electronic band structure of TiSe₂ (Ref. 13) has been reproduced in Fig. 1; it may be interpreted in terms of the ETBM interpolation. On the whole the wave functions in the energy range of the valence bands are predominantly derived from selenium orbitals. The Γ_3^- and A_3^- states at the Fermi energy consist of selenium p_x and p_y orbitals, the dispersive $\Gamma_2^- - A_2^-$ band has Se p_z character. The almost flat $\Gamma_3^+ - A_3^+$ band is characterized by bonding orbitals of Se p_x , p_y and Ti d_{xy} , $d_{x^2-y^2}$ type, and the lowest $\Gamma_1^+ - A_1^+$ band consists of Se p_z orbitals with some admixture of Ti $d_{3z^2-r^2}$ orbitals.

III. PHOTOEMISSION THEORY

A. General aspects

In the following section a brief outline of the photoemission theory is given, starting with the well-known "golden-rule" formula¹⁹ for the photocurrent measured at a point $\mathbf{R}$ ($\mathbf{R} = R\hat{\mathbf{R}}$) far outside the sample:

$$R^2 j_r(\mathbf{R}, E) = -\frac{1}{8\pi^2} v_e \sum_m \delta(E - E_m) \left| \frac{1}{c} \mathbf{A} \cdot \langle \Phi^*(\hat{\mathbf{R}}, E + \omega) | \mathbf{p} | m \rangle \right|^2. \quad (1)$$

v_e is the velocity of the photoelectron outside the sample. The electron is assumed to be excited from the initial state $|m\rangle$ at energy $E = E_m$ to the final state (i.e., the time-reversed LEED state) $|\Phi^*(\mathbf{R}, E + \omega)\rangle$ at energy $E + \omega$ by an electromagnetic wave with a vector potential $\mathbf{A}$. The summation in (1) is restricted to all occupied states m . As we shall treat the normal-emission geometry only, the relevant symmetry group is C_{3v} . The LEED state must transform according to the trivial representation of this group. Therefore only transitions from valence states of symmetry E induced by p_x and p_y or transitions from states of symmetry A_1 induced by the operator p_z are allowed in view of the dipole matrix element in (1). Thereby the z axis of the coordinate system is assumed to point in the direction of the surface normal.

Let ξ denote the angle between the surface normal and the direction of incidence of the p -polarized light wave, then the golden-rule formula takes the form

$$R^2 j_r(\mathbf{R}, E) = -\frac{1}{8\pi^2 c^2} |\mathbf{A}|^2 v_e [(\sin^2 \xi) J_{\perp} + (\cos^2 \xi) J_{\parallel}] . \quad (2)$$

The quantities J_{pol} , with $\text{pol} = \parallel$ or $\perp$, are defined by

$$J_{\parallel} = \sum'_m \delta(E - E_m) |\langle \Phi^* | p_x | m \rangle|^2 \quad (3)$$

and

$$J_{\perp} = \sum'_m \delta(E - E_m) |\langle \Phi^* | p_z | m \rangle|^2 . \quad (4)$$

Obviously the ΓA photocurrent is invariant under rotation of the specimen around the surface normal. In this approximation corrections to the electromagnetic field at the surface, caused by the dielectric response of the solid, have been neglected. However, we have also tried to account for this effect in a very crude way replacing the vector potential $\mathbf{A}$ in (1) by the vector potential $\mathbf{A}'$ calculated from a frequency-dependent dielectric constant $\epsilon(\omega)$ with the aid of the classical Fresnel formulas.²⁰ The corresponding results will be discussed in Sec. V.

With the definition $p_{\parallel} := p_x$ and $p_{\perp} := p_z$ the formulas (3) and (4) can be condensed into

$$J_{\text{pol}} = \sum'_m \delta(E - E_m) |\langle \Phi^* | p_{\text{pol}} | m \rangle|^2 . \quad (5)$$

$$J_{\text{pol}} = -\frac{1}{\pi} \text{Im} \sum_{vv'} \sum_{n\tau\mu} \sum_{n'\tau'\mu'} T_v T_{v'}^* \langle \psi^*(E + \omega, k_{\perp v}) | p_{\text{pol}} | \mathbf{k}_{\parallel} = 0, n\tau\mu \rangle \mathcal{G}_{nn'}(z)_{\tau\mu, \tau'\mu'} \times \langle \mathbf{k}_{\parallel} = 0, n'\tau'\mu' | p_{\text{pol}} | \psi^*(E + \omega, k_{\perp v'}) \rangle . \quad (11)$$

The matrix-element integrals occurring in (11) can be reduced to those of the uppermost layer $n = 1$ by means of the Bloch property of the final-state wave functions, leaving us with a vector of matrix elements having the following components:

$$M_{\text{pol}}(E + \omega, k_{\perp v})_{\tau\mu} = \langle \psi^*(E + \omega, k_{\perp v}) | p_{\text{pol}} | \mathbf{k}_{\parallel} = 0, n = 1, \tau\mu \rangle^* . \quad (12)$$

The restriction of the summation to occupied states has been dropped, therefore the curves for J_{pol} have to be cut explicitly at the Fermi energy after the computation of (5) has been completed. In (5) the retarded Green's operator $G'(E)$ can be substituted for the sum over all states $|m\rangle$ in combination with the δ function selecting the energy. We get

$$J_{\text{pol}} = -\frac{1}{\pi} \text{Im} \langle \Phi^* | p_{\text{pol}} G'(E) p_{\text{pol}} | \Phi^* \rangle . \quad (6)$$

Within the tight-binding theory applied to the valence states the layer Bloch waves

$$\langle \mathbf{r} | \mathbf{k}_{\parallel} n \tau \mu \rangle = \frac{1}{(N_{\parallel})^{1/2}} \sum_{\mathbf{R}_{\parallel}} e^{i\mathbf{k}_{\parallel} \cdot (\mathbf{R}_{\parallel} + \tau)} u_{\mu}(\mathbf{r} - \mathbf{R}_{\parallel} - n\mathbf{c} - \tau) \quad (7)$$

constructed from atomic orbitals u_{μ} centered at atomic positions in the n th layer serve as a nonorthogonal basis set. The lattice vectors $\mathbf{R}_{\parallel}$ run over all $N_{\parallel}$ primitive cells in one Se-Ti-Se sandwich, and τ is a vector which points to a specific atom within the unit cell. The Bloch vector $\mathbf{k}_{\parallel}$ parallel to the layers is set to zero because we deal with normal emission. Conjugate states $|\mathbf{k}_{\parallel} n \tau \mu\rangle$ are introduced by

$$\langle \mathbf{k}_{\parallel} n \tau \mu | \mathbf{k}'_{\parallel} n' \tau' \mu' \rangle = \delta_{\mathbf{k}_{\parallel} \mathbf{k}'_{\parallel}} \delta_{nn'} \delta_{\tau\tau'} \delta_{\mu\mu'} . \quad (8)$$

With respect to this conjugate basis the matrix representation of the Green's operator is

$$\mathcal{G}_{nn'}(z)_{\tau\mu, \tau'\mu'} = \langle \mathbf{k}_{\parallel} = 0, n \tau \mu | G(z) | \mathbf{k}_{\parallel} = 0, n' \tau' \mu' \rangle . \quad (9)$$

Insertion of the expansion of the LEED state in terms of conduction-band Bloch states $|\psi^*(E + \omega, k_{\perp v})\rangle$ (with complex z components $k_{\perp v}$ of the corresponding wave vectors),²¹ i.e.,

$$|\Phi^*\rangle = \sum_v T_v^* |\psi^*(E + \omega, k_{\perp v})\rangle , \quad (10)$$

into Eq. (6) yields the following expression for the currents J_{pol} (with $z = E + i\eta$, $\eta = 0^+$):

The additionally appearing Bloch factors $e^{ik_{\perp}nc}$ are combined with the Green's function to give an expression of the following type:

$$\Gamma(z, k_{\perp}, k'_{\perp}) := \sum_{nn'=0}^{N_{\perp}-1} e^{-ik_{\perp}^*nc} \mathcal{G}_{nn'}(z) e^{ik'_{\perp}nc} . \quad (13)$$

This matrix contains all information about both the valence density of states and the relaxed wave-vector

selection rule (with regard to final-state wave-vector components $k_{\perp}$ and $k'_{\perp}$). Combination of Eqs. (11)–(13) finally yields the result

$$J_{\text{pol}} = -\frac{1}{\pi} \text{Im} \sum_{\nu\nu'} T_{\nu} T_{\nu'}^* e^{-ik_{\perp\nu}c + ik_{\perp\nu'}^*c} \mathbf{M}_{\text{pol}}(E + \omega, k_{\perp\nu})^+ \times \Gamma(z, -k_{\perp\nu}^*, -k_{\perp\nu'}^*) \times \mathbf{M}_{\text{pol}}(E + \omega, k_{\perp\nu'}) . \quad (14)$$

B. Calculation of Γ

As stated above, the empirical tight-binding method is used for the description of the valence states. The transfer matrix $\mathcal{H}(\mathbf{k})_{\tau\mu, \tau'\mu'} = \langle \mathbf{k}\tau\mu | H | \mathbf{k}\tau'\mu' \rangle$ and the overlap matrix $\mathcal{L}(\mathbf{k})_{\tau\mu, \tau'\mu'} = \langle \mathbf{k}\tau\mu | \mathbf{k}\tau'\mu' \rangle$ are defined with regard to Bloch functions that are derived from atomic orbitals analogously to the layer Bloch waves in (7):

$$\langle \mathbf{r} | \mathbf{k}\tau\mu \rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot (\mathbf{R} + \boldsymbol{\tau})} u_{\mu}(\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}) . \quad (15)$$

The valence-band structure of the bulk can then be calculated by solving the generalized eigenvalue problem $[\mathcal{H}(\mathbf{k}) - E(\mathbf{k})\mathcal{L}(\mathbf{k})] \cdot \mathbf{c}(\mathbf{k}) = 0$. With the abbreviation

$$\mathcal{G}_{\nu}(z)_{\tau\mu, \tau'\mu'} := e^{i\kappa_{\nu}(\tau_z - \tau'_z)} [\mathcal{Z}\mathcal{L}(\mathbf{p}) - \mathcal{H}(\mathbf{p})]_{\tau\mu, \tau'\mu'}^{-1} \Big|_{\mathbf{p}=(0, \kappa_{\nu})} \quad (16)$$

(with $\kappa_{\nu} = 2\pi\nu/N_{\perp}c$) the Green's function of an $N_{\perp}$ -layer slab with periodic boundary conditions, expressed as a matrix with respect to the basis of layer Bloch waves defined in Eq. (7), may be written as

$$\mathcal{G}_{nn'}^{(0)}(z) = \frac{1}{N_{\perp}} \sum_{\nu=0}^{N_{\perp}-1} e^{i\kappa_{\nu}c(n-n')} \mathcal{G}_{\nu}(z) . \quad (17)$$

The (001) surface of the specimen is incorporated in the tight-binding model by applying a method^{22,23} that has been used by Pollman *et al.* in the case of semiconductor surfaces. The Green's function of a slab with the layer at $n=0$ missing can be derived from the bulk value $\mathcal{G}_{nn'}^{(0)}$ by

$$\mathcal{G}_{nn'}(z) = \mathcal{G}_{nn'}^{(0)}(z) - \mathcal{G}_{n0}^{(0)}(z) \mathcal{G}_{00}^{(0)}(z)^{-1} \mathcal{G}_{0n'}^{(0)}(z) . \quad (18)$$

If the damping of the final-state wave functions is sufficiently high, the summation in (13) may be extended to infinity. Insertion of (18) into (13) then leads to

$$\Gamma(z, k_{\perp}, k'_{\perp}) = \mathcal{G}^0(z, k_{\perp}^*, k'_{\perp}) - \mathcal{G}^+(z, k_{\perp}^*) \mathcal{G}_{00}^{(0)}(z)^{-1} \mathcal{G}^-(z, k'_{\perp}) , \quad (19)$$

with the matrices $\mathcal{G}^0$ and $\mathcal{G}^{\pm}$ defined by

$$\mathcal{G}^0(z, k_{\perp}^*, k'_{\perp}) := \frac{1}{N_{\perp}} \sum_{\nu=0}^{N_{\perp}-1} \frac{1}{1 - e^{i(\kappa_{\nu} - k_{\perp}^*)c}} \times \frac{1}{1 - e^{-i(\kappa_{\nu} - k'_{\perp})c}} \mathcal{G}_{\nu}(z) , \quad (20)$$

and

$$\mathcal{G}^{\pm}(z, k_{\perp}) := \frac{1}{N_{\perp}} \sum_{\nu=0}^{N_{\perp}-1} \frac{1}{1 - e^{\pm i(\kappa_{\nu} - k_{\perp})c}} \mathcal{G}_{\nu}(z) . \quad (21)$$

The single summation in Eq. (20) or (21) has to be carried out numerically. It replaces the double summation in (13).

C. Calculation of the matrix elements

For the determination of the matrix elements (12) we are faced with integrals

$$\langle \psi^*(E + \omega, k_{\perp\nu}) | p_{\text{pol}} | \mathbf{k}_{\parallel} = 0, n = 1, \tau\mu \rangle = \frac{1}{(N_{\parallel})^{1/2}} \sum_{\mathbf{R}_{\parallel}} \int \psi(E + \omega, k_{\perp\nu}, \mathbf{r}) p_{\text{pol}} u_{\mu}(\mathbf{r} - \mathbf{R}_{\parallel} - \mathbf{c} - \boldsymbol{\tau}) d\mathbf{r} . \quad (22)$$

The sum in (22) gives a factor $N_{\parallel}$, the number of unit cells per layer, because ψ is invariant with respect to translations with a lattice vector parallel to the surface ($\mathbf{k}_{\parallel} = 0$). Furthermore, it is sufficient to retain only that part of the integrand which is totally symmetric with respect to the point group C_{3v} . This yields:

$$\langle \psi^*(E + \omega, k_{\perp\nu}) | p_{\text{pol}} | \mathbf{k}_{\parallel} = 0, n = 1, \tau\mu \rangle = (N_{\parallel})^{1/2} \int \psi(E + \omega, k_{\perp\nu}, \mathbf{r}) \left[\frac{1}{6} \sum_{T \in C_{3v}} P(T) [p_{\text{pol}} u_{\mu}(\mathbf{r} - \mathbf{c} - \boldsymbol{\tau})] \right] d\mathbf{r} . \quad (23)$$

Atomic wave functions are tabulated by Clementi and Roetti.²⁴ As they are given in an analytical form, they can be inserted in Eq. (23) and the term in large parentheses can be evaluated. This yields functions $\chi_{lm}(\mathbf{r} - \mathbf{c} - \boldsymbol{\tau})$ that can be written as a sum of two terms, each of them being the product of a radial function and a spherical harmonic. These two terms correspond to the two channels of allowed dipole transitions from an atomic state with angular momentum quantum number l to states with $l' = l \pm 1$. To summarize, integrals of type

$$m_{\tau lm} = \int \psi(E + \omega, k_{\perp\nu}, \mathbf{r}) \chi_{lm}(\mathbf{r} - \mathbf{c} - \boldsymbol{\tau}) d\mathbf{r} \quad (24)$$

have to be calculated.

The direct numerical treatment of this three-dimensional integral would be much too time consuming. In order to derive an approximation we split the above expression into three terms,

$$m_{\tau lm} = m_{\tau lm}^{(\text{mt})} + m_{\tau lm}^{(\text{fe})} + m_{\tau lm}^{(\text{sc})} \quad (25)$$

(where mt denotes muffin-tin sphere, fe free electron, and sc scattering corrections), which can all be reduced to some one-dimensional integrals. For the definition of these terms see Fig. 3 showing the division of the domain of integration in (24) into subdomains. $\Omega_0^{(\tau)}$ denotes the

FIG. 3. Division of space in subdomains which is used for the construction of the muffin-tin potential. The function χ_{lm} centered at $\tau + \mathbf{c}$ overlaps with neighboring muffin-tin spheres $\Omega_{(\tau_n)}^{(\tau)}$.

muffin-tin sphere centered around the atom of $\tau + \mathbf{c}$, and $\Omega_{\tau_1}^{(\tau)}$, etc. are the muffin-tin spheres of the neighboring atoms.

(1) The term $m_{\tau lm}^{(mt)}$ is defined by the integral (24), the domain of integration being restricted to the muffin-tin sphere $\Omega_0^{(\tau)}$. Like χ_{lm} the final-state wave functions ψ are also given as an expansion around the center at $\tau + \mathbf{c}$ by means of the LEED calculation

$$\begin{aligned} \psi(E + \omega, k_{\perp v}, \mathbf{r}) \\ = \sum_{lm} A_{lm}(\tau, k_{\perp v}, E + \omega) \phi_l(E + \omega, |\mathbf{r} - \tau - \mathbf{c}|) \\ \times Y_{lm}(\Omega(\mathbf{r} - \tau - \mathbf{c})), \end{aligned} \quad (26)$$

with angular momentum $l \leq l_{\max}$. Therefore in spherical polar coordinates the angular integrations are trivial because the spherical harmonics are orthonormal.

(2) The second term $m_{\tau lm}^{(fe)}$ is defined by

$$m_{\tau lm}^{(fe)} = \int_{R^3/\Omega_0^{(\tau)}} \psi^{(fe, \tau)}(E + \omega, k_{\perp v}, \mathbf{r}) \chi_{lm}(\mathbf{r} - \mathbf{c} - \tau) d\mathbf{r}. \quad (27)$$

$\psi^{(fe, \tau)}$ is represented by an expansion in the same way as ψ in (26), but with ϕ_l replaced by $(e^{2i\delta_l} h_l^{(1)} + h_l^{(2)})/2$, the free-electron wave function that matches the radial part of the scattering wave function at the muffin-tin radius smoothly. Just like in the previous case the angular part of the integral is performed yielding the orthogonality condition with respect to the quantum numbers l and m . The convergence of the integral (27) is guaranteed by the exponential decay of the functions χ_{lm} . For the calculation of the coefficients A_{lm} in (26) only moderately damped plane wave components of ψ in the interstitial region between the atomic scattering planes have been taken into account.

(3) The difference between the exact result $m_{\tau lm}$ and the quasi-atomic-part $m_{\tau lm}^{(mt)} + m_{\tau lm}^{(fe)}$ is caused by the deviation of $\psi^{(fe, \tau)}$ from the correct LEED wave function ψ outside the central muffin-tin sphere. The largest contribution ought to be caused by the deviation from the free-

electron behavior brought about by the atomic scattering potential in the neighboring muffin-tin spheres within the same Se-Ti-Se sandwich. Therefore we set

$$m_{\tau lm}^{(sc)} = \sum_n' \int_{\Omega_{(\tau_n)}^{(\tau)}} (\psi - \psi^{(fe, \tau)}) \chi_{lm}(\mathbf{r} - \mathbf{c} - \tau) d\mathbf{r}. \quad (28)$$

For the expression $\psi - \psi^{(fe, \tau)}$ we get an expansion of type (26) around the center at $\mathbf{c} + \tau + \tau_n$ by an extension to the standard LEED theory. The functions χ_{lm} are also expanded around these neighboring centers:

$$\begin{aligned} \chi_{lm}(\mathbf{r} - \mathbf{c} - \tau) = \sum_{l'm'}^{(\tau_n)} \chi_{lm, l'm'}^{(\tau_n)}(|\mathbf{r} - \mathbf{c} - \tau - \tau_n|) \\ \times Y_{l'm'}(\Omega(\mathbf{r} - \mathbf{c} - \tau - \tau_n)). \end{aligned} \quad (29)$$

The calculation of the expansion coefficients $\chi_{lm, l'm'}^{(\tau)}(\mathbf{r})$ is quite tedious and time consuming, but this is of minor importance as these values have to be tabulated only once after the start of the program and not for every single photon or binding energy separately. After insertion of (29) into (28) the angular integrations are carried out immediately as above. Thus even the scattering correction term (28) can be calculated numerically by means of few one-dimensional integrations.

D. The photoemission program

The photoemission theory sketched above has been applied to the (001) surface of 1T-TiSe₂ and some details of the corresponding numerics are given in this paragraph. The program consists of an initial section for the tabulation of several parameters (Clebsch-Gordan coefficients, tight-binding transfer and overlap matrices, wave function, e.g., $\chi_{lm, l'm'}$ for $l' \leq 5$, etc.) and a section in which the currents J_{pol} are calculated, containing an outer loop for all photon energies and an inner loop for all binding energies. The photocurrent R^2j , itself is calculated according to Eq. (2) in a separate program, allowing a fast treatment of different geometries concerning the light incidence without the necessity of recalculating J_{pol} .

With fixed final-state energy E_{CB} relative to the muffin-tin zero the phase shifts δ_l and the corresponding atomic scattering wave functions $\phi_l(r)$ are calculated for $l \leq l_{\max} = 7$ using routines published by Pendry.²¹ With a set of his LEED subprograms²¹ the complex band structure and the plane wave coefficients of the LEED state are determined. Several variables not occurring in the standard LEED program, such as the expansion coefficients A_{lm} , are computed from the LEED data by additional subroutines. 19 reciprocal lattice vectors are included in the set of LEED beams, dividing up into six subsets of symmetry equivalent beams in the case of normal incidence. The difference between the muffin-tin zero and the Fermi energy is set to $\Delta E = 4.5$ eV. (Assuming a value of ≈ 5.7 eV for the work function²⁵ this yields ≈ 10 eV for the real part of the optical potential.) Similarly to the work by Grandke *et al.*²⁶ the imaginary part of the optical potential is assumed to be energy dependent according to

$$\text{Im } V_0(E_{\text{CB}}) = -0.3 - \frac{2.4}{1 + e^{-[E_{\text{CB}}/(\text{eV}) - 26.1]/1.8}} \quad (30)$$

in eV. The increase in $-\text{Im}V_0$ accounts for the additional damping caused by plasmon creation, the energetic position has been chosen in view of the plasmon frequency of TiS_2 .²⁷ The orders of magnitude given by Eq. (30) are in accordance with the energy dependence of the absorption potential in MoS_2 and NbSe_2 as discussed by Smith.²⁸

In the next step the matrix Γ is calculated, starting from our tight-binding interpolation for a slab with $N_1=80$ Se-Ti-Se layers. The Bloch functions in the basis set are constructed from the titanium $3d$ and the selenium $4p$ orbitals. The values of the transfer and overlap parameters have been changed with respect to previous fits^{14,29,30} in order to improve both the correspondence with the *ab initio* band structure¹³ and the description of the wave functions of the valence electrons. The imaginary part of the complex energy $z=E+i\eta$ is fixed at $\eta=0.2$ eV. An increase in η mainly has the same effect on the spectra as a convolution with a corresponding Lorentzian curve. In the last step the matrix elements are computed and $J_{\parallel}$ and $J_{\perp}$ are determined according to Eq. (14). Thereby it proved sufficient to include in the summation only those three conduction-band Bloch waves which are weakly damped.

The photoemission program outlined above is based on the same level of approximation for the photoemission process (i.e., single-particle model, optical potential, inclusion of matrix elements) as Pendry's well-known photoemission code PEOVER.^{31,32} In contrast to his program we need not recompute the valence-band structure of our substance by means of a Korringa-Kohn-Rostoker-like method (which would require an excellent effective single-particle potential), but instead we use a fast and simple ETBM interpolation, which has also been applied to other problems.³⁰ It is possible to investigate the influence of the surface on the photocurrent by replacing $\mathcal{G}(z)$ by the corresponding bulk value $\mathcal{G}^{(0)}(z)$ in the expression for Γ . Moreover, Eq. (14) allows an interpretation of the results within the model of weighted indirect transitions proposed by Grandke *et al.*²⁶

IV. CRYSTAL PREPARATION AND PHOTOEMISSION EXPERIMENT

Single crystals of 1T-TiSe₂ were grown from the elements by iodine vapor transport in closed quartz tubes. We used an excess of selenium of 1.5 and 3.0 mg/cm³ reaction chamber volume, a temperature gradient of 640–540°C, and a growth time of 45 d. These preparation conditions are known to yield the best obtainable stoichiometry. Structure, orientation, and quality of the samples were controlled by standard x-ray techniques and by LEED. The high stoichiometry is indicated by the resistivity ratio $\rho(180\text{ K})/\rho(300\text{ K})$ of at least 3 and by the photoemission experiment itself, i.e., the extremely weak emission from the titanium $3d$ -type band around the L point of the Brillouin zone.

For the photoemission measurements the crystals were mounted on an adjustable sample holder and cleaved in ultra-high vacuum of about 10^{-8} Pa. The photoemission spectra were taken with synchrotron radiation from the

DORIS II storage ring at Hamburger Synchrotronstrahlungslabor in Hamburg in the region $8 < \hbar\omega < 30$ eV. The electrons were detected by use of a 180° spherical analyzer mounted on a goniometer, which is movable independently around two axes (improved Leybold Heraeus 3-DARES). This experimental setup allows a very accurate final sample adjustment. The direction of normal emission was adjusted with an accuracy of $\Delta k_{\parallel}=0.01\text{ \AA}^{-1}$ by taking photoemission spectra (excited with He I resonance radiation) in small-angle steps around the critical point without moving the sample. For the spectra shown here an overall energy resolution of $\Delta E \approx 100$ meV and an angular resolution of $\pm 0.5^\circ$ were chosen.

V. RESULTS AND DISCUSSION

A series of experimental photoemission spectra in the photon energy regime $27.9 \geq \hbar\omega \geq 12.4$ eV ($445 \leq \lambda \leq 1000$ Å) is shown in Fig. 4. The spectra are normalized with respect to their absolute maxima. Only the background of inelastically scattered electrons has been subtracted (similar to the Shirley method³³). All peaks are associated with the Se p -type valence-band states and enumerated by capital letters. The dispersion of the peaks results from three-dimensional effects in these quasi-two-dimensional crystals, owing to interactions not only parallel but also perpendicular to the layers. Results with respect to the experimental and theoretical band structure are discussed elsewhere.⁸ The photoemission spectra shown in Ref. 8 were taken with a high-energy resolution over a small energy regime from the Fermi level up to a binding energy of 2 eV in order to resolve the spin-orbit splitting of the uppermost Se $4p$ valence band, which is important for demonstrating the small indirect band overlap of about 100 meV and the semimetallic character of 1T-TiSe₂. The spectra shown in Fig. 4, however, cover a much wider energy range, and as we do not discuss any fine structure near the Fermi level in this paper, the spectra taken with this resolution are quite sufficient.

In order to compare with the experimental data, the theoretical spectra are shown in the left panel of Fig. 4. Emission from all valence bands is found in the spectra and, as the bands do not overlap in the ΓA direction, the peaks can unambiguously be assigned to the corresponding valence states. The nondispersive $\Gamma_3^+-A_3^+$ bands give rise to the maxima labeled *A* and *C* in the figure, which are fixed near the Fermi energy and at a binding energy of 3 eV. The dispersion of the peak *B* derived from the $\Gamma_2^--A_2^-$ band is in accordance with the direct transition model¹⁴ and it is also correctly reproduced by the full theory presented here. (One exception, *B''*, is considered below.) Therefore, we shall concentrate here especially on intensities and their variation with photon energy, i.e., the information contained in the spectra beyond the peak positions. In what follows, the term intensity always means relative intensity, as all spectra have been scaled independently.

In the experimental data a distinct minimum in the intensity of peak *C* is observed at $\lambda=620$ Å. A similar but less pronounced behavior occurs in the theoretical spectra near $\lambda=655$ Å. In general, the relative intensities of

the maxima *A* and *C* get significantly smaller in favor of an enhanced intensity of the peaks *B* and *D* at higher photon energies.

The (dispersive) peak *B'* in the theoretical spectra at small photon energies is not assigned to the peak *B''* in

the experimental data because the latter one is clearly nondispersive. Therefore we have proposed the alternative explanation that this peak is due to electronic states induced by Frenkel defects near the surface.³⁰ The maximum *B* disperses from the Fermi level at $\lambda = 850 \text{ \AA}$ down

FIG. 4. Calculated (left section) and experimental (right section) ΓA photoemission spectra for various wavelengths λ of the incident uv light (angle of incidence $\xi = 33^\circ$, no correction of the vector potential A , $\eta = 0.2 \text{ eV}$). The maxima *A*–*D* are discussed in the text.

to -3 eV at $\lambda=540$ Å, thereby increasing much in intensity. The incorrect energetic position of this peak in the 540-Å spectrum is caused by the width of the p_z band, which comes out too large in the valence-band calculations, thereby calling for refined *ab initio* computations. With increasing photon energy the structure B shifts back to the Fermi level, and both in experiment and theory we find two peaks B and B' in this energy regime. Finally, the photoemission maximum with the largest binding energy, denoted D in Fig. 4, is derived from the $\Gamma_1^+-A_1^+$ valence band. The double structure D', D'' , well resolved in the experimental spectrum with $\lambda=655$ Å, is also found in the calculated results. It has been explained by a coupling to different final-state Bloch waves in a previous paper.¹⁴ Again the small intensities increase with $\hbar\omega$, the peak D becoming dominant in the high-energy spectra.

To this extent it has been possible to predict the relative intensities in the normal-emission energy-distribution curves for TiSe_2 . This has been achieved in spite of the one-dimensional density of states which may be characterized as a doubly spiked curve with a small background, as explained in the Introduction. Furthermore, Eq. (14) leads us to an interpretation of the results within the weighted indirect transition model by Grandke *et al.* In a previous work³⁴ the expression $-e^{2\text{Im}k_{\perp}c} \text{Im}\Gamma(z, -k_{\perp}^*, -k_{\perp}^*)_{jj}$ containing information about the one-dimensional density of states and the $k_{\perp}$ selection rule has been examined and, on the whole, the maxima of this quantity could be assigned to direct transitions, with deviations becoming noticeable in the high-energy high-damping regime. Furthermore, we can infer from our calculations that the scattering corrections $m_{r/lm}^{(sc)}$ are generally small, not altering the structure of the spectra. In order to demonstrate the influence of the surface (with regard to the initial states) on the spectra, a spectrum calculated according to the full theory is compared to another one which was calculated with the Green's function $\mathcal{G}$ replaced by the bulk Green's function $\mathcal{G}^{(0)}$ in Fig. 5. As the layer resolved one-dimensional density of states flattens near the surface, the square-root singularities of the bulk disappear in the topmost layer. Thus it is not surprising that an increased emission near the band edges is observed in Fig. 5 when "switching off" the surface. This emphasizes the necessity of including surface effects even if there are no surface resonances or surface states.

As to the remaining differences one may seek for possible improvements of the photoemission calculation. Besides many-body effects, which do not seem to be numerically tractable in general, one source of deviation lies in the scattering potential and the wave functions. It might be removed by inserting a better potential, including non-muffin-tin corrections for example, or by replacing the ETBM interpolation by an *ab initio* calculation.

FIG. 5. Influence of the surface on the photoemission spectra (parameter $\xi=33^\circ$, $\eta=0.1$ eV). Solid line: results calculated with $\mathcal{G}$ replaced by $\mathcal{G}^{(0)}$, i.e., the change of the valence states near the surface is neglected. Dashed line: results calculated with the full theory.

However, this would complicate the calculation considerably. On the other hand, the vector potential of the light wave incident on the specimen has not been corrected for the dielectric response of the solid, which may be too crude an approximation. Photoemission spectra have been measured for angles of incidence of the light $\vartheta=33^\circ$ and $\vartheta=52^\circ$ showing only minor differences, especially at higher photon energies ($\lambda \approx 500$ Å). This result contradicts Eq. (2), which leads to intensity variations that are governed by the prefactors $\sin^2\xi$ and $\cos^2\xi$. In a first attempt to solve this problem we have inserted the vector potential derived from the classical Fresnel formulas into the expression for the photocurrent, using a crude model for the dielectric constant of TiSe_2 [based on $\epsilon(\omega)$ for TiS_2 (Ref. 27)]. In this case the dependence of the theoretical spectra on the angle of incidence of the light wave is much smaller. However, it is not yet clear which details of the electromagnetic field at the surface³⁵ have to be included in case of TiSe_2 in order to retain a sufficient input for the vector potential used in the photoemission calculation.

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