Polarized x-ray-absorption spectra of TiS$_2$, TiSe$_2$, and TiTe$_2$

S. Bocharov, G. Dräger, and D. Heumann
Fachbereich Physik der Martin-Luther-Universität Halle-Wittenberg, Friedemann-Bach-Platz 6, D-06108 Halle, Germany

A. Šimůnek and O. Šipr
Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 16200 Praha 6, Czech Republic

We studied the anisotropy of the unoccupied electron states of three titanium dichalcogenides by means of polarized x-ray-absorption spectroscopy. The experimental spectra of TiS$_2$, TiSe$_2$, and TiTe$_2$ at the Ti K edge and of TiTe$_2$ at the Te L$_1$ edge were compared with the results of real-space multiple-scattering calculations. The local angular momentum projections of the densities of states at the titanium sites are presented for energies up to 25 eV above the Fermi level. The Ti K-edge spectra of all three dichalcogenides are quite similar to each other provided the differences in their lattice constants are suppressed by comparing the spectra in equivalent energy scales. However, the correspondence between the Te L$_1$ edge of TiTe$_2$ and the S K edge of TiS$_2$ is much less pronounced. For most of the spectra good agreement between experiment and theory was found. [S0163-1829/98/01336-8]

I. INTRODUCTION

The titanium dichalcogenides TiS$_2$, TiSe$_2$, and TiTe$_2$ crystallize in the trigonal space group with one formula unit in the unit cell. Their crystal structure can be considered as a sandwich consisting of chalcogen-Ti-chalcogen slabs. The slabs are internally strongly bonded, but only weakly coupled to each other. This feature allows us to create intercalated sublayers, which could be useful for some technological applications. That is one of the reasons why the electronic structure of titanium dichalcogenides has been the subject of an intensive study lately. The differences between the electronic structure of TiS$_2$ and TiSe$_2$ were investigated theoretically by Fang, de Groot, and Haas.\textsuperscript{1} Photoemission spectroscopy studies were published by Bodicker and Schattke\textsuperscript{2} for TiSe$_2$ and by Claessen \textit{et al.}\textsuperscript{3} for TiTe$_2$.

For the understanding of this weak bonding mechanism an analysis of the lowest unoccupied electron states can be helpful. Much effort was devoted to x-ray-absorption spectroscopy studies\textsuperscript{3-7} of TiS$_2$ or of Li$_2$TiS$_2$ intercalates.\textsuperscript{8} However, to our knowledge no published study included a comparison of results for different titanium dichalcogenides, which definitely must correlate with each other and thus prove or negate the adopted conclusions.

In this work we present results of electron state studies by means of the polarized Ti K x-ray-absorption spectroscopy for a range of titanium dichalcogenides (TiS$_2$, TiSe$_2$, and TiTe$_2$). Because of the site symmetry the lowest unoccupied electron states projected on the Ti atom split into $p_{x,y,z}$, $d_{x^2-y^2}$, $d_{xy}$, $d_{x^2-y^2}$, $d_{z^2}$, and $d_{xy}$-like groups in these compounds. Due to the original experimental technique,\textsuperscript{9,10} we were able to separate the spectral components arisen from these different symmetry-resolved groups. The spectral components are considered to reproduce approximately the density of the lowest empty electron states projected on the Ti atom. Saying "approximately" we bear in mind effects such as finite initial and final states lifetimes, device smearing, and also the influence of radial transition matrix elements.

II. SPECTRAL ANALYSIS

Here we briefly describe some theoretical foundations of the extracting of symmetry-resolved partial spectral components. We investigate absorption of photons by electrons in solids. Within the one-electron approximation, the absorption coefficient $\mu$ can be determined as the probability of electron transition from an initial core state (with wave function $\psi_i$ and energy $E_i$) to a final unoccupied state (with wave function $\psi_f$ and energy $E_f$)

$$\mu(h\omega, \mathbf{e}, \mathbf{k}) = \sum |\langle \psi_f | e^{i\mathbf{k} \cdot \mathbf{r}} \psi_i \rangle|^2 \delta(E_f - E_i - h\omega),$$

where $h\omega$ is the photon energy and $\mathbf{e}$ and $\mathbf{k}$ are the polarization and the wave vectors of the absorbed photon, respectively. The summation involves all initial and final states that have the energy difference of $h\omega$.

In further analysis, we concentrate on the case of K-edge absorption, hence the initial-state wave function $\psi_i$ is $R_0 Y_{00}$. Note that this core wave function is practically nonzero only close to the center of the absorbing atom. The final-state wave function $\psi_f$ can be angularly projected onto the same atom, hence in the region of interest it can be written as a superposition of atomiclike wave functions with definite angular momenta.

$$\psi_f(\mathbf{r}) = \sum_{l,m} R_l(r) Y_{lm}(\hat{r}).$$

Here $R_l(r)$ and $Y_{lm}(\hat{r})$ represent radial and angular parts of the wave function, respectively.

In Eq. (1) we consider the first two terms of the expansion $e^{i\mathbf{k} \cdot \mathbf{r}} = 1 + i\mathbf{k} \cdot \mathbf{r} + \cdots$, i.e., we take into account electric dipole and quadrupole terms only (other terms do not contribute to x-ray spectra significantly). As the dipole and quadrupole term amplitudes do not interfere, we can rewrite\textsuperscript{12} the formula (1)
\( \mu(h \omega, \mathbf{e}, \mathbf{k}) \propto \delta(E_f - E_i - h \omega) \sum_{l,m} \left( |\langle R_l Y_{lm}| \mathbf{e} \cdot \mathbf{r} | R_0 Y_{00} \rangle|^2 \right) \\
+ \frac{1}{2} |\langle R_l Y_{lm}| \mathbf{e} \cdot \mathbf{r} \cdot \mathbf{k} | R_0 Y_{00} \rangle|^2 \right). \) 

(3)

Inserting the mathematical expressions for the angular parts of the wave functions, one can obtain the absorption coefficient as the sum of dipole and quadrupole components \( \mu = \mu_D + \mu_Q \), where

\[
\mu_D \propto p_x e_x^2 + p_y e_y^2 + p_z e_z^2,
\]

\[
\mu_Q \propto d_{x_2} (e_x k_x + e_y k_y)^2 + d_{y_2} (e_y k_x + e_z k_z)^2 + d_{z_2} (e_z k_x + e_x k_y)^2 + e_x k_x^2 + d_{x_2} e_y (e_y k_y - e_z k_z)^2 + \sqrt{3} d_{z_2} (e_z k_x)^2.
\]

This means that each polarized spectrum can be interpreted as a weighted sum of partial symmetry-resolved components. Each of the components is formed only by the transitions to orbitals with a definite angle momentum. The factors \( p_x, p_y, p_z, d_{x_2}, d_{y_2}, d_{z_2}, d_{x_2} e_y, \) and \( d_{z_2} \) represent the so-called partial spectral components, i.e., the densities of states with a definite orbital symmetry modulated by the radial transition probability. We assume the radial matrix elements are equal for all states with equal angular number \( l \) and change with energy only insignificantly. The expressions in parentheses in Eq. (4) (combined from the projections of the vectors \( \mathbf{e} \) and \( \mathbf{k} \) and taken in the power of 2) are the coefficients by these components and are determined just by the actual experimental setting. We call these coefficients partial spectral weights.

Therefore, by measuring three spectra (each of them represented by the absorption coefficient \( \mu \)) with different orientations I, II, and III of vector \( \mathbf{e} \) relative to the crystal structure, one can use the expression (4) to set up an appropriate system of linear equations and extract the partial-density components \( p_x, p_y, \) and \( p_z \):

\[
\mu^I \propto p_x (e_x^2)^2 + p_y (e_y^2)^2 + p_z (e_z^2)^2,
\]

\[
\mu^II \propto p_x (e_x^2)^2 + p_y (e_y^2)^2 + p_z (e_z^2)^2,
\]

\[
\mu^III \propto p_x (e_x^2)^2 + p_y (e_y^2)^2 + p_z (e_z^2)^2,
\]

(5)

\[
\begin{pmatrix}
   p_x \\
   p_y \\
   p_z
\end{pmatrix} \propto 
\begin{pmatrix}
   (e_x^2)^2 \\
   (e_y^2)^2 \\
   (e_z^2)^2
\end{pmatrix}^{-1}
\begin{pmatrix}
   \mu^I \\
   \mu^II \\
   \mu^III
\end{pmatrix},
\]

provided the quadrupole contributions can be neglected. The superscripts in Eq. (5) distinguish between three independent spectra recorded for different sample orientations. In the case of titanium dichalcogenides, the states \( p_x \) and \( p_y \) are degenerated and the linear system (5) has an order of 2.

Thus, if linearly polarized radiation is absorbed, then in the process of dipole transitions \( 1s \rightarrow p_{x,y,p_z} \), the partial spectral weights of the two \( p \) states will depend on the orientation of the \( p_{x,y} \) or \( p_z \) orbitals with respect to the polarization vector of the absorbed radiation. In the case of quadrupole transitions \( 1s \rightarrow d_{x_2} e_y, d_{x_2} e_y, d_{z_2} e_y, d_{z_2} \), the partial spectral weights will depend on the orientation of the orbitals with respect to the polarization vector and the wave vector as well. The electron transitions described above take into ac-
In the zero position \((\varphi = 0, \theta = 0, \psi = 0)\) the threefold axis of the trigonal crystal structure coincides with the x-ray beam direction \(\mathbf{k}\). All spectra were normalized on the equivalent effective sample thickness.

In order to separate the absorption resulting from \(K\) transitions exclusively, we used a background subtraction. The background function \(f(E) = a/E^4 + b/E^3 + c\) after Victoreen shows acceptable results.

### IV. THEORY

Polarized Ti \(K\)-edge x-ray absorption near-edge structure (XANES) spectra of \(\text{TiS}_2\), \(\text{TiSe}_2\), and \(\text{TiTe}_2\) as well as polarized Te \(L_1\)-edge XANES of \(\text{TiTe}_2\) were calculated employing the real-space–multiple-scattering (RS–MS) formalism.\(^1\) We used a modified ICXANES computer code of Vvedensky, Saldin, and Pendry.\(^12\) The calculations presented here were performed for clusters of 135 atoms for the Ti edges and of 138 atoms for the Te edge, implying that the radii of these clusters varied between 8.3 and 9.6 \(\text{Å}\) according to the compound and/or selected edge. Exploratory XANES calculations for a whole series of smaller cluster sizes were performed to verify that a convergence with respect to the number of included atoms had been achieved.\(^7\)

The largest angular momentum included in the single-site scattering was \(L_{\text{max}} = 4\). Test calculations for all four edges with \(L_{\text{max}}\) as large as 6 were done for clusters of 25 atoms with hardly any difference visible.

Non-self-consistent muffin-tin potentials were generated via the so-called Mattheiss prescription (superposition of charge densities of isolated atoms). An energy-independent \(X_a\) exchange–correlation potential with the Kohn-Sham value of \(\alpha = 2/3\) was used.\(^13\) Structural data for \(\text{TiS}_2\), \(\text{TiSe}_2\), and \(\text{TiTe}_2\) were taken from the CRYSTIN database.\(^14\)

Muffin-tin radii of nonoverlapping spheres were determined so that the “matching potential condition” is satisfied. The muffin-tin zero was set to the average interstitial potential. We verified for the particular case of the \(\text{TiS}_2\) spectrum that identifying the muffin-tin zero with the value of the inner-sphere potential at the boundaries of muffin-tin spheres (minimizing thus the step in the potential, as suggested, e.g., in Ref. 15) does not change the results significantly even close the absorption edge. Hence we believe that the results presented here are sufficiently robust with respect to the technical details of muffin-tin potential construction (note that the opposite case would point to the unsuitability of the muffin-tin approximation itself).

The influence of the core hole left by the excited electron was taken into account while calculating atomic charge densities by removing one electron from the core level and putting it into the lowest unoccupied atomic level (“relaxed and screened approximation”; see Ref. 16 for a more detailed analysis). Again, for \(\text{TiS}_2\) we checked that there was practically no difference between our XANES spectra calculated with and without a core hole.

Theoretical results presented in this paper include broadening by an energy-dependent Lorentzian of full width at half maximum \(w = w_c + 0.10(E - E_F)\). The constant part \(w_c\) accounts for the core hole lifetime and is 0.94 and 3.32 eV for the Ti \(K\) edge and the Te \(L_1\) edge, respectively.\(^17\) The energy-dependent term represents inelastic energy losses of the photoelectron of energy \(E\) (the “Fermi energy” \(E_F\) is identified with the onset of a prepeak for our purpose). This simple ansatz formula proved to be efficient both in metallic\(^18\) and in nonmetallic\(^19\) materials. We will return to the question of inelastic energy losses in Sec. VI.

### V. RESULTS

To study the contribution of Ti \(1s \rightarrow d\) transitions, we performed several measurements in such experimental settings in which the dipole contributions to the spectra (determined by their partial spectral weights) were always the same, while the quadrupole contributions varied.\(^8\) The differences between spectra recorded for these sample orientations (see, for example, the first two orientations in Table I) did not exceed the experimental error limits of about 1% of the total intensity. Therefore, we suppose that the contribution of Ti \(1s \rightarrow d\) transitions is too small to be detected with the available equipment in all three investigated compounds. With this assumption we interpret the spectra as a composition of merely the Ti \(1s \rightarrow p_{x,y}\) and \(1s \rightarrow p_z\) absorptions. If the assumption is not valid then extraction procedures according to the relation (5) performed for different combinations of spectra will provide inconsistent curves of partial components \(p_{x,y}\) or \(p_z\). On the other hand, the coincidence of all curves in the groups \(p_{x,y}\) and \(p_z\) can serve as a criterion of the reliability of the technique as well as of the validity of the simplifications and assumptions used. The partial spectral weights in the absorption process for \(p_{x,y}\), \(p_z\), \(d_{3z^2-r^2}\), \(d_{xy, x^2-y^2}\), and \(d_{z^2}\) are displayed in Table I for all sample orientations used in the experiments.

The results of the \(\text{TiS}_2\) analysis show rather good consistency. Four spectra by different sample orientations were measured and are displayed in Fig. 3(a).

In Fig. 3(b) we present the partial spectral components

### Table I. Weight coefficients in the absorption process of all symmetry-resolved orbitals for different sample orientations.

<table>
<thead>
<tr>
<th>Sample position</th>
<th>(p_{x,y})</th>
<th>(p_z)</th>
<th>(d_{3z^2-r^2})</th>
<th>(d_{xy, x^2-y^2})</th>
<th>(d_{z^2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\varphi = 0, \theta = 0, \psi = 0)</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\varphi = 0, \theta = 45, \psi = 0)</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>(\varphi = 0, \theta = 0, \psi = 45)</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td>(\varphi = 0, \theta = 0, \psi = 22.5)</td>
<td>0.854</td>
<td>0.146</td>
<td>0.5</td>
<td>0.125</td>
<td>0.375</td>
</tr>
<tr>
<td>(\varphi = 0, \theta = 36, \psi = 29)</td>
<td>0.846</td>
<td>0.154</td>
<td>0.346</td>
<td>0.423</td>
<td>0.231</td>
</tr>
<tr>
<td>(\varphi = 0, \theta = 32.7, \psi = 32.7)</td>
<td>0.793</td>
<td>0.207</td>
<td>0.294</td>
<td>0.396</td>
<td>0.310</td>
</tr>
<tr>
<td>(\varphi = 0, \theta = 0, \psi = 30)</td>
<td>0.75</td>
<td>0.25</td>
<td>0.25</td>
<td>0.188</td>
<td>0.562</td>
</tr>
</tbody>
</table>
FIG. 3. (a) Polarized Ti K absorption spectra of TiS$_2$ recorded for four different sample orientations, together with (b) the partial spectral components extracted from three different alternative sets of the experimental spectra. In the “zero position” ($\varphi = \theta = \phi = 0$) the trigonal axis $c$ coincides with the wave vector $\mathbf{k}$ and the axis $a$ is parallel to the polarization vector $\mathbf{e}$ (see Fig. 1).

$p_{x,y}$ and $p_z$ extracted from three independent sets of spectra measured at different sample orientations. The equivalent curves obtained from the alternative sets are displayed all together in order to emphasize the reproducibility of the technique.

Analogously to TiS$_2$, five different Ti K absorption spectra were recorded for TiSe$_2$ [Fig. 4(a)]. The resulting $p_{x,y}$ and $p_z$ components are very similar with those of TiS$_2$. The only difference is that a better sample quality allowed us to perform one more additional independent measurement and thus to reach a better statistics. In order to compensate for the influence of thickness effects, we applied such sample orientations as arguments in free-electron propagators $A$, viz., as arguments in free-electron propagators $A$.

TiTe$_2$ offers a more complicated situation. Here the Te $L_1$ absorption edge lies very close to that of the Ti K absorption. Nevertheless, the Te $L_1$ absorption must be predominantly formed by the dipole transitions $2s \rightarrow p$. From the trigonal surrounding of the Te atom one can expect a similar polarization dependence as for Ti K absorption. Therefore, the extraction of partial components from the common spectrum involving both the Te $L_1$ and the Ti K absorption edges will provide the summarized components $\text{Ti} \ p_{x,y} + \text{Te} \ p_{x,y}$ and Ti $p_z + \text{Te} \ p_z$. The absorption edges are situated so that the Ti K absorption begins at about 4960 eV while the Te $L_1$ absorption begins at about 4930 eV, where the XANES of the Te $L_1$ absorption is nearly over [see Fig. 5(a)]. In Fig. 5(b) we present the partial spectral components extracted from the common Te $L_1$ and Ti K absorption spectra of TiTe$_2$.

All the investigated compounds have nearly identical geometrical structures; they differ just by a uniform bond-length scaling. Hence, in comparing spectra of TiS$_2$, TiSe$_2$, and TiTe$_2$, one can make use of the fact that interatomic distances $R_{ij}$ enter the XANES formula only in combination with energy $E$ measured from the muffin-tin zero $V_{MTZ}$, viz., as arguments in free-electron propagators $A$. That means that if XANES spectra in consideration are scaled appropriately, any differences due to different lattice constants will be removed: One can immediately see that if two particular spectral features occur at energies $E_1$ and $E_1'$ for one compound and at energies $E_2$ and $E_2'$ for another compound, then neglecting differences in phase shifts one gets

$$ (E_1 - E_1') R_1^2 = (E_2 - E_2') R_2^2, \quad (6) $$

where $R_1$ and $R_2$ are characteristic interatomic distances in the first and in the second compound, respectively. Any deviations still remaining after such a scaling can be attributed to differences in phase shifts, i.e., in the electronic structure.

In Table II nearest-neighbor distances and corresponding scaling factors according to the relation (6) are presented (we}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nearest-neighbor distance (Å)</th>
<th>Scaling factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiS$_2$</td>
<td>2.42</td>
<td>1.000</td>
</tr>
<tr>
<td>TiSe$_2$</td>
<td>2.53</td>
<td>0.915</td>
</tr>
<tr>
<td>TiTe$_2$</td>
<td>2.73</td>
<td>0.786</td>
</tr>
</tbody>
</table>
choose a unity scaling factor for TiS\textsubscript{2} by definition). These scaling factors were employed to determine equivalent energy ranges used for displaying experimental as well as theoretical results for TiS\textsubscript{2}, TiSe\textsubscript{2}, and TiTe\textsubscript{2} Ti K-edge spectra in Fig. 6. The positioning of theoretical spectra in the absolute photon energy scale was set by convenience for each edge, so that the best agreement with corresponding experimental curves is achieved.

In Fig. 6(c) the theoretical Ti K edge of TiTe\textsubscript{2} is superposed onto the Te L\textsubscript{1} EXAFS (see below). It barely differs from a “pure” Ti K edge; therefore, a separate Ti K-edge calculation is not presented here. The only feature introduced by the presence of the Te L\textsubscript{1} edge is the occurrence of the low-energy tail below the prepeak in the p\textsubscript{z} component (around $E=4962$ eV). For all three compounds, a full convergence of the calculation with respect to cluster sizes was achieved at 99 atoms; however, gross features of the full-cluster theoretical spectra were reproduced for 51 atoms already.

Experimental and theoretical Te L\textsubscript{1}-edge polarized spectra of TiTe\textsubscript{2} are compared in Fig. 7, together with analogous data for the S K edge of TiS\textsubscript{2} taken from the literature.\textsuperscript{5,7} Note that both of these spectra probe unoccupied $p$ states as “seen” from the anion site. Again, energy ranges of the plots were scaled according to Table II. As the experimental and theoretical S K-edge spectra of Ref. 5 are not polarized, we included in Fig. 7 also calculated projected densities of unoccupied states published by Šimůnek et al.\textsuperscript{7}

The onset of the Ti K edge is shown in the figure as well. The energy separation between the theoretical Ti and Te edges (27 eV) was taken over from the measured spectra, while the ratio between the calculated intensities of the Te and Ti edges was provided by the theory itself.

The two main peaks at 4941 and 4950 eV can be reproduced (with a correct polarization dependence) for a cluster containing 16 atoms. On the other hand, even 57 atoms was not enough to generate the second peak splitting, which appears only for yet larger clusters.

VI. DISCUSSION

Titanium dichalcogenides TiS\textsubscript{2}, TiSe\textsubscript{2}, and TiTe\textsubscript{2} show a very similar behavior with respect to the process of the polarized x-ray absorption. There is an apparent correlation between spectral features of the three compounds and nearly each qualitative conclusion is valid in all three cases simultaneously. In particular the energy separation between the prepeaks and the main peaks as well as between the main peaks and the second peaks are roughly identical for all three compounds, provided the energy scaling according to Eq. (6) is taken into account (see Fig. 6).

The real-space multiple-scattering calculation reproduces the measured spectra quite well both in peak positions and in polarization dependence. For TiS\textsubscript{2}, it compares better than the calculations of Antonangeli et al.\textsuperscript{4} This contradiction is a bit surprising, given the fact that Antonangeli et al. use a method similar to ours. Nevertheless, it is difficult to identify the reasons for this as no details regarding the size of the cluster or scattering potential are given in Ref. 4. Note, however, that angular momentum projected densities of both occupied and unoccupied states of TiS\textsubscript{2} calculated recently by a pseudopotential method\textsuperscript{7} or by a full-potential linearized augmented-plane-wave method\textsuperscript{30} disagree with the results presented by Antonangeli et al.\textsuperscript{4} as well.

The prepeak at 4968 eV in Ti K-edge spectra of titanium dichalcogenides\textsuperscript{6,7} and related compounds\textsuperscript{21} has been the subject of an intensive study. Our analysis clearly demonstrates that the quadrupole contribution to this prepeak is negligible for all three investigated compounds. Otherwise, one would never reach such a good coincidence in the polarization decomposition performed for different “sets” of spectra, taking into account the dipole $1s-p$ transitions only...
Regarding the polarization dependence of the prepeak, Šimůnek et al.⁷ argue on basis of self-consistent electronic structure calculations that in TiS₂ the first subpeak appears in the $p_{x,y}$ polarization only, while the second one is isotropic. Our experimental data for TiSe₂ and TiTe₂ suggest that this conclusion might be valid for the other two layered dichalcogenides as well.

The largest discrepancy between the theoretical and experimental curves occurs within the region above the main peak for all three compounds (in the region 4980–4985 eV). The occurrence of a redundant structure at this energy seems to be a general drawback of all calculations: for TiSe₂ it appears in the RS-MS results of Wu et al.⁶ as well as in self-consistent band-structure calculations of Šimůnek et al.⁷

The disagreement is most prominent for the $p_z$ component in TiS₂, where it is hardly possible to find any experimental counterpart to the theoretical peak at 4982 eV. Interestingly, the same feature, which is apparently redundant in TiS₂, appears both in the calculated and, less pronounced but still distinct, in the experimental spectrum of TiSe₂. Hence there seems to be a sufficient reason to believe that the suppression of the fine structure around 4981–4983 eV in TiS₂ is a many-body effect and that this effect is not the same in TiS₂ and in TiSe₂. The simple linearly energy-dependent Lorentzian broadening clearly is not good enough to account for this fact.

The Te $L_1$-edge polarized spectrum of TiTe₂ is compared with the unpolarized S K-edge spectrum of TiS₂ in Fig. 7. The energy range available for comparing the two spectra is quite small in comparison to the Ti K spectra in Fig. 6. As a consequence, one cannot judge unambiguously whether or not there is an overall similarity between the TiS₂ and TiTe₂ anion spectra. The spectra resemble each other in the beginning: The separation between the first peak at 2468 eV (TiS₂) or 4941 eV (TiTe₂) and the second one (at 2476 eV for TiS₂ and 4947 eV for TiTe₂) is very similar in both compounds, provided the energy scaling of Eq. (6) is taken into account (cf Fig. 7). Also the polarization dependence of the Te $L_1$ edge in TiTe₂ is the same as the computed polarization dependence of the S K edge in TiS₂: i.e., the first peak is higher for the $p_{x,y}$ polarization than for the $p_z$ symmetry, while the second peak is more or less isotropic. This polarization feature ought to persist at the Te edge as well: We display in Fig. 7 the polarized densities of states broaden by a Lorentzian with a full width at half maximum (FWHM) equal to both 0.59 eV (lower curves, corresponding to the S K edge) and 3.32 eV (upper curves, corresponding to the Te $L_1$ edge). On the other hand, the third peaks (at 2487 eV for TiS₂ and at 4952 eV for TiTe₂) differ in their positions quite a lot so they do not seem to be analogous to one another.

The first peak is distinctly split in TiS₂, both in the experiment and in the theory.⁴,⁵,⁷ The separation of sub-peaks is 2 eV. A similar splitting occurs in our RS-MS calculation for TiTe₂ for very large cluster sizes (more than 60 atoms) as well and the same is true also for projected Te $p$ density of states derived from the self-consistent band-structure calculation of Claessen et al.⁵ However, due to different core hole widths (3.32 eV for the Te $2s$ level compared to 0.59 eV for the S $1s$ level⁷), such a splitting cannot be present in the TiTe₂ experimental spectrum.

A not-so-perfect coincidence between the experimental
polarized curves extracted from different data sets at Te $L_1$ absorption edge (cf. Fig. 5) could be caused by experimental errors or (less probably) may indicate the presence of a non-negligible quadrupole contribution. The fact that there is less of a correspondence between anion edges than between cation ones is not surprising: When comparing cation edges (Fig. 6), the absorbing atom is always the same, viz., titanium, while it changes from S to Te for anion edges (Fig. 7). Hence it is natural to expect that the differences in electronic structure would have a better chance to get revealed through anion edges than through cation ones.

VII. CONCLUSIONS

The results of the comparative analysis of the three titanium dichalcogenides could be summarized in the following points. The main spectral peaks and polarization features in x-ray-absorption spectra of TiS$_2$, TiSe$_2$, and TiTe$_2$ can be reproduced by a real-space multiple-scattering calculation within a one-electron theory. The good agreement between polarized spectra obtained from different data sets as well as between the experimental and the theoretical curves for each compound demonstrate the suitability and usefulness of our procedure for the polarization decomposing.

The Ti $K$-edge spectra of all three compounds are qualitatively quite similar to each other, especially if the differences in lattice constants are diminished by comparing them in the equivalent energy scales. This is really true for the trends in polarization dependence, in particular in the case of the prepeak. Some quantitative differences between spectra of different compounds still persist after the scaling, thus manifesting differences in the electronic structure. Specifically there is evidence that many-body effects underlying photoelectron inelastic energy losses are different in TiS$_2$ and TiSe$_2$ and are responsible for suppression of the fine structure between 4980 and 4985 eV in Ti $K$-edge XANES of TiS$_2$.

As far as the Te $L_1$-edge spectrum of TiTe$_2$ and the S $K$-edge spectrum of TiS$_2$ are concerned, again some similarities between them can be seen. However, clear differences between them persist even after energy scaling, especially beyond the absorption edge.

ACKNOWLEDGMENTS

The experimental work was supported by the Hamburger Synchrotronstrahlungslabor HASYLAB (Project No. II-95-67). The theoretical work was supported by Grant No. A 1010608 of the Academy of Sciences of the Czech Republic and Grant No. 202/97/0566 of the Grant Agency of the Czech Republic. The use of the CRYSTIN crystallographic database was supported by Project No. 203/96/0111 of the Grant Agency of the Czech Republic.

17 F. Al Shamma, M. Abbate, and J. C. Fuggle, in Unoccupied Electronic States (Ref. 11), p. 348.