Unoccupied electron states of TiS_2 studied by means of polarized x-ray absorption

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Using polarized x-ray-absorption spectroscopy along with band-structure and real-space multiple-scattering calculations, we have studied unoccupied states of TiS_2 . With respect to titanium and sulfur sites, the local angular momentum projections of the density of states are presented for states up to 25 eV above the Fermi level. Good agreement between experiment and theory suggests that quadrupole ($1s \rightarrow d$) transitions in Ti K absorption are negligible compared to dipole ($1s \rightarrow p$) transitions. We have applied a new technique for construction of pseudopotentials adapted to the chemical bond and found that previous calculation of electronic states with energies higher than 10 eV above Fermi level was not correct. [S0163-1829(97)03044-0]

I. INTRODUCTION

TiS_2 has a layered crystal structure consisting of sulfur-titanium-sulfur slabs. Each slab is formed by a two-dimensional hexagonal titan sublattice sandwiched by two closely adjacent sulphur hexagonal sublattices. The sulfur-titanium bonds are quite strong within a single slab. On the other hand, there is only a weak coupling between individual slabs and, therefore, positive ions can be intercalated into the gaps between the (S-Ti-S) slabs. It is important to obtain as much information as possible on the lowest unoccupied states, which are most likely involved in the intercalation process. For that reason, TiS_2 and also other lamellar transition-metal dichalcogenides have attained considerable attention.¹⁻³

The first polarized Ti K absorption of TiS_2 was studied by Antonangeli *et al.*,⁴ however, their theoretical results do not match well the experiment and cannot reliably explain and interpret observed features in spectra. Quite recently Wu *et al.*⁵⁻⁷ presented unpolarized experimental and theoretical studies of x-ray-absorption near-edge structure (XANES) of Ti K and S K edges for TiS_2 . Experimental data were interpreted by means of the full multiple-scattering (MS) theory and tight-binding linear muffin-tin orbital (LMTO) band-structure method. They also presented Ti p -, Ti d -, and S p -projected densities of states and used group theory for symmetry analysis of the lowest unoccupied orbitals (t_{2g} and e_g bandlike states). Also in Ref. 7, the polarized spectra measured by Antonangeli *et al.*⁴ were analyzed within the MS theory in the pre-edge region.

Considering anisotropy and two-dimensional character of the slabs, we applied polarized x-ray absorption to bring additional information about the local symmetry of unoccupied electron states in the energy range $0 < E < 25$ eV above the Fermi energy. In this paper we present polarized Ti K -absorption edges for the $\mathbf{e} \perp \mathbf{z}$ and for $\mathbf{e} \parallel \mathbf{z}$ components of the Ti K spectrum ($\mathbf{e}$ is the polarization vector of the x rays, $\mathbf{z}$ is perpendicular to the x, y plane of the S-Ti-S slab). The polarized components are compared to theoretical results ob-

tained by the real-space multiple-scattering technique and to the results of the pseudopotential band-structure method. Additionally all local partial densities of s , (p_x, p_y) , p_z , d_{z^2} , $(d_{xy}, d_{x^2-y^2})$, and (d_{xz}, d_{yz}) states are projected on both the Ti and S atoms. Our calculations are compared with earlier Ti K - and S K -edge results of Wu *et al.*^{6,7} and with polarized results of Antonangeli *et al.*⁴

II. EXPERIMENT

If a linearly polarized radiation is absorbed, the absorption process depends on the mutual orientation of the sample and the polarization vector $\mathbf{e}$ of the absorbed radiation. The theoretical analysis of the absorption coefficient provides a mathematical expression depending generally on the polarization $\mathbf{e}$ and wave vector $\mathbf{k}$. This dependence allows us to extract "partial absorptions" related to local (p_x, p_y) , p_z , (d_{xz}, d_{yz}) , $(d_{xy}, d_{x^2-y^2})$, and d_{z^2} -like states from polarized spectra measured with different mutual orientations of $\mathbf{e}, \mathbf{k}$ vectors and the crystal axes orientations. This technique was described by Dräger and co-workers^{8,9} and was applied here for the Ti K -absorption spectra.

TiS_2 plates of about $2 \times 2 \times 0.02$ mm³ with trigonal axis oriented perpendicular to the cleavage planes were used as the absorption single-crystal samples.¹⁰ The orientation and crystal quality were proved by means of the Laue pattern. The experiments were carried out at the beam line E4 (HASYLAB, Hamburg) equipped with an x-ray focusing mirror and a Si(111) double-crystal monochromator. The sample plates were positioned in a PC-controlled goniometer allowing three perpendicular rotations ϕ , θ , and Ψ (see Fig. 1) so that any sample orientation with respect to $\mathbf{e}$ and $\mathbf{k}$ vectors of the synchrotron radiation can be achieved.

Comparison of spectra recorded with sample orientations of equal dipole weights [in the transitions $1s \rightarrow (p_x, p_y)$ and $1s \rightarrow p_z$] but different quadrupole weights [$1s \rightarrow (d_{xz}, d_{yz})$, $1s \rightarrow (d_{xy}, d_{x^2-y^2})$ and $1s \rightarrow d_{z^2}$] display experimental differences not larger than 1% of the whole intensity. To illustrate this point, in Fig. 2 we show the spectra for two sample orientations for which the weights of (p_x, p_y) , p_z states are

FIG. 1. Scheme of the experimental arrangement (the polarization vector $\mathbf{e}$ lies in the plane of the storage ring).

equal in both cases and amount to 1, 0, respectively, while the weights of (d_{xz}, d_{yz}) , $(d_{xy}, d_{x^2-y^2})$, and d_{z^2} states amount either 1, 0, 0 (for $\phi=0^\circ$, $\theta=0^\circ$, $\Psi=0^\circ$) or 0.5, 0.5, 0 (for $\phi=0^\circ$, $\theta=45^\circ$, $\Psi=0^\circ$). Thus, even from the experimental results alone one can suppose that the probability of the $1s \rightarrow d$ quadrupole transition is much smaller than the probability of the dipole $1s \rightarrow p$ transition.

The fact of absence of any considerable d -related contributions in the recorded spectra allows to discriminate only between (p_x, p_y) - and p_z -related dipole parts of spectra. Calculation of partial weights makes it possible to resolve pure (p_x, p_y) and p_z densities of states from several spectra recorded with different sample orientations. The polarized absorption spectra obtained in this way from three different data sets are presented in Fig. 3 (note a very good coincidence of all three pairs of curves).

III. THEORY

A. Real-space multiple-scattering approach

Polarized Ti K -edge XANES spectra of TiS_2 were calculated employing the real-space multiple-scattering (RS-MS)

formalism using an amended computer code of Vvedensky *et al.*¹¹ The calculations presented here were performed for a cluster of 135 atoms and the largest angular momentum included in the single-site scattering was $\ell_{\max}=4$ —both these limits were checked for convergence. A non-self-consistent muffin-tin potential was generated via the so-called Mattheiss prescription (superposition of charge densities of isolated atoms). 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 that by setting it to the value of the potential at the boundaries of muffin-tin spheres (minimizing thus the step in the potential) does not change the results significantly.

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 Ti $1s$ level and putting it into the lowest unoccupied atomic level (“relaxed and screened approximation”). However, there was practically no difference between our XANES spectra calculated with and without the core hole.

B. Band-structure calculations

The electronic structure of TiS_2 has been calculated by a self-consistent pseudopotential method within the local-density theory. We have used a plane-wave basis that imposes no shape approximations on either the charge density or the potential and fully reflects the symmetry of the space group D_{3d}^3 and the anisotropy of the crystal. At first we generated the sulfur and titan pseudopotentials by the phase-shift technique¹² for the ground-state electron configuration of free atoms. The resulting density of states (DOS) for occupied states was in a good agreement with other calculations,^{13–15} however, the calculated Ti K -absorption spectrum was in *disagreement* with experiment. The same

FIG. 2. Polarized Ti K -absorption spectra of TiS_2 recorded for two sample orientations that induce identical dipole but different quadrupole transition probabilities. Defined by the three angles ϕ , θ , and Ψ , in “zero position” the trigonal axis c coincides with wave vector $\mathbf{k}$ and the axis a is parallel to the polarization vector $\mathbf{e}$ (see Fig. 1).

FIG. 3. Polarized Ti K spectra of TiS_2 : (p_x, p_y) and p_z components are resolved from three alternative sets of spectra. Here all (p_x, p_y) components are drawn with thicker lines.

happened when we used standard pseudopotentials,¹⁶ i.e., occupied states of TiS_2 were calculated correctly but unoccupied states were not. This indicates that the ground state or ionic configuration¹⁶ used for generation of pseudopotential of titanium does not produce a pseudopotential having an energy width of transferability sufficient for the energies above the Fermi level.

Conventionally, problems of this kind have been circumvented by “guessing” a suitable atomic configuration for creation of the convenient pseudopotential. Instead of such an approach, we used the crystal charge density of TiS_2 obtained by standard pseudopotentials mentioned above and applied iterative technique described in detail by Vackář, Šimůnek, and Podlůcky.¹⁷ The basic idea of this technique is that we can construct a pseudopotential from crystal charge density and use it in a standard self-consistent band-structure calculation producing new crystal charge density. This new charge density is then used for a construction of a new pseudopotential, i.e., the iterative loop is closed. When the convergency in the crystal charge density and pseudopotential is reached then the final pseudopotentials (we performed this procedure for both titanium and sulphur potentials simultaneously) are adapted to a given crystal structure and interatomic bonds. In this way the p component of the titanium pseudopotential is also created, i.e., the problem with the unoccupied $3p$ level in a free Ti atom is naturally solved. As a matter of fact, the accuracy in the symmetry character of the electron states is crucial particularly for p -like states since the p -like states of titanium are created by the sulfur-titanium bond and the dipole transition matrix element selects these states in the case of the Ti K spectra.

The technical details of the calculations of the x-ray spectra in the pseudopotential formalism were described in detail elsewhere.¹⁸ Here we note that the radial part of the dipole matrix element is approximated by a constant and the angular part of it uses the plane-wave basis set mentioned above.

The symmetry of the space group D_{3d}^3 subdivides the p functions into two groups, (p_x, p_y) and p_z , and the d -like functions into three groups, d_{z^2} , $(d_{xy}, d_{x^2-y^2})$ and (d_{xz}, d_{yz}) . With respect to these groups the angular dependent local-projected densities of states were also calculated.

IV. RESULTS AND DISCUSSION

Our experiment and both calculations of the Ti K absorption are presented in Fig. 4. The calculated spectra were convoluted with a Lorentzian of the width about 1 eV corresponding to the natural width of the Ti $1s$ hole. The zero of the energy scale coincides with the calculated Fermi energy

FIG. 4. Experimental and theoretical Ti K-edge polarized XANES spectra of TiS_2 . Components with $e \parallel xy$ plane are drawn with solid lines; components with $e \parallel z$ axis are drawn with broken lines. The zero of energy axis coincides with the Fermi energy of the band-structure calculation, the vertical scale is arbitrary.

of TiS_2 . The experiment and RS-MS calculation were aligned to the band-structure spectrum so that the best agreement between them is obtained.

We did not apply other smearing to take into consideration instrumental effects. Consequently the calculated curves show more detail than the experiment.

In the case of the xy component (full lines in Fig. 4), we observe a very good accordance between both the theoretical curves and also good agreement with the experimental one. The positions and relative intensities of the pre-edge peak at 0–5 eV and the following peaks at about 10 eV and 22 eV are well reproduced by both calculations — the only exception being a too high intensity of the peak at 22 eV in the band-structure calculation. Compared to the xy components, the z components (dashed lines) show lower intensities at 0–5 eV, lower intensities of the first main peak at 10 eV, and higher intensities in the interval 13–20 eV. All these features are qualitatively observable in measured and calculated z components and also in the earlier measurement of Antonangeli *et al.*⁴ There is no obvious counterpart in the experimental spectrum to the fine structure appearing between 15 eV and 19 eV at both theoretical calculations. A similar “false” structure in this energy range was obtained also by Wu *et al.*⁷ These weak features seem to be smeared out in the experiment by inelastic effects.

Both calculations of spectra, band-structure and RS-MS techniques, are performed in the dipole approximation for the $\text{Ti } 1s \rightarrow \text{Ti } p$ -like empty states transitions and the reasonable agreement between theory and experiment shows that unoccupied $\text{Ti } p$ states dominate in the $\text{Ti } K$ spectrum. However, the x-ray absorption, being a local and symmetry selective process, does not provide full information about electronic structure. To analyze the angular character of all unoccupied states, we have calculated the projected densities of states (PDOS). The band-structure calculations of the electronic density of states is projected on the Ti site and S site in Fig. 5 and Fig. 6, respectively. In both figures the attention should be given to the vertical scales since the relative ratio of s -, p -, and d -like densities significantly differ.

The Ti projected DOS in Fig. 5 shows that in the pre-edge energy region 0–5 eV the local angular character is d like. From the quantitative point of view the p -like states are here negligible in comparison with d states, however, they create the main part of the $\text{Ti } K$ -absorption intensity in this pre-edge region. Consequently, the quadrupole $\text{Ti } 1s \rightarrow 3d$ transitions are insignificant, in contrast to a very high density of d states, and the polarization dependence is governed by the (p_x, p_y) and p_z components. This finding agrees well with the outcome of orientation-dependence analysis of the measured spectra mentioned in Sec. II.

We see in Fig. 4 in both calculations and experiment that the angle-dependent behavior displays only the feature at 2 eV but not at 4 eV. Figure 5 clearly shows the peak in the p_x density at 2 eV, which is missing in the p_z . Therefore, the origin of the pre-peak feature at 2 eV has to be attributed to the (p_x, p_y) states created on the Ti atoms by bonds with neighboring atoms. The finding that the features in the pre-edge region can be interpreted in terms of mixing the Ti atom p and neighboring $\text{Ti } d$ orbitals in xy plane was quite recently realized by Wu *et al.*⁷ on the basis of a different technique — they applied a full MS calculation at the Ti

FIG. 5. Angular-projected local PDOS of TiS_2 at the Ti site. Note different vertical scales for particular graphs.

K edge by using different clusters containing various numbers of shells coordinating the central Ti atom.

Using the simple language of molecular orbitals, the $\text{Ti } d$ states are split by the octahedral field into the t_{2g} and e_g levels. The local partial analysis given in Fig. 5 additionally shows the local orbital composition of these two levels: the d_{z^2} and $(d_{xy}, d_{x^2-y^2})$ states contribute mainly to t_{2g} , while e_g consists predominantly of (d_{xz}, d_{yz}) states.

In Fig. 6 we present the sulfur projected densities of states. The lowest valence band between energies -13.3 and -11.3 eV arises from the $3s$ sulfur electrons and is located beyond the energy scale of all figures. As expected, the d -like states can be completely neglected compared to the s and p components. The only remarkable polarization feature is the varying intensity of the peak at $E \sim 3-4$ eV in the p PDOS, otherwise the difference between the p_x and p_z -states is not significant. For completeness of our work and for comparison with the measurement and MS calculations of Wu *et al.*,⁶ we present our calculation and their results in Fig. 7. We see that the double structure of the S K edge at about 2 and 4 eV is well reproduced by our band-structure results. The energy difference between the two peaks is practically the same as the MS result of Wu⁶ (at about 3.7 eV), the experimental value is about 4.0 eV. The second maxima in the 10–12 eV region are also pro-

FIG. 6. Angular-projected local PDOS of TiS_2 at the S site. Note different vertical scales for particular graphs.

duced by both theories; the fine structure seems to be smeared in the measured curve.

It is interesting to note that the electron states in the 0–5 eV energy region have very different local orbital projections—they have mainly Ti d -like character and, on the other

FIG. 7. Experimental and theoretical S K -edge XANES spectra of TiS_2 . The zero of energy axis coincides with the Fermi energy of the band-structure calculation; the vertical scale is arbitrary. The experiment and the RS-MS calculation are taken from Ref. 6.

hand, mainly S s - and p -like character. This fact clearly indicates their bandlike character and the appropriate description by the band-structure approach. That means that the qualitative description of these states by means of the hybridization of the Ti $3d$ and S $3p$ states or the description by means of the configuration interaction can be avoided.

The bandlike approach gives us a natural and, additionally, a quantitative description, however, it can fail in the region of higher energies above the Fermi level. As mentioned in Sec. III B, this really happened to us when we used inadequate atomic configurations for the construction of the Ti pseudopotentials: we obtained very high Ti p -like PDOS for states above 10 eV compared to states in the Ti pre-edge region in the 0–5 eV energy range. As a matter of fact, the Ti p -projected DOS derived from LMTO band-structure calculations of Wu *et al.*⁷ also appears to be incorrect above 10 eV and does not match the experimental data. The LMTO result produces the main peak of the Ti p PDOS at 14 eV (correct energy is 10 eV) and its magnitude is too high compared to pre-edge densities, cf. Fig. 7 of Wu *et al.*⁷ The failures in both calculations of the Ti p -like states can be understood by the fact that the p states in free Ti atom are not occupied and they originate due to the nonspherical interaction with neighboring atoms in chemical bond.

V. CONCLUSION

By means of polarized x-ray-absorption spectroscopy, as well as band-structure and real-space multiple-scattering calculations, we have interpreted Ti K - and S K -absorption edges of TiS_2 . We have performed local angular momentum analysis of the electron states of TiS_2 in the energy range $-7 < E < 25$ eV, where zero in the energy scale corresponds to the Fermi level. The main results of our investigation can be summarized as follows.

(1) The two polarized components of the Ti K spectrum agree quantitatively well with both calculations performed in dipole approximation for the Ti $1s \rightarrow p$ transitions. Accordingly, the quadrupole Ti $1s \rightarrow d$ transitions are insignificant despite the fact that Ti d -like density of electron states is high.

(2) In the case of S K -absorption spectrum there is a good agreement between our band-structure calculation and previous experimental and multiple-scattering results of Wu *et al.*^{5,6} Our local angular momentum analysis shows that anisotropy of the sulfur p states is small. The only possibly observable polarization effect in the S K -absorption spectrum is the varying intensity of the second of the “main peaks” at $E \sim 3$ –4 eV above the edge.

(3) We have found that the standard pseudopotential or LMTO band-structure techniques do not describe Ti p -like states correctly in the energy range 10 eV above the Fermi level. This failure can be overcome by applying a new iterative technique for construction of Ti pseudopotential from crystal charge densities, which is adapted to TiS_2 crystal structure and Ti-S bonds.

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