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#### Experimental and theoretical studies of the electronic structure of $\text{TiS}_2$

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Sulfur  $K$ - and titanium  $L_{2,3}$ -edge absorption spectra of transition-metal disulfide,  $\text{TiS}_2$ , were measured using x-ray-absorption spectroscopy (XAS) and electron-energy-loss spectroscopy (EELS), respectively. All features in the experimental spectra are very well reproduced by full multiple-scattering-theory calculations. Combined analysis of theoretical and experimental XAS and EELS spectra, and linear muffin-tin orbital band-structure calculations, tend to demonstrate that  $\text{TiS}_2$  is a semimetal. [S0163-1829(96)51932-6]

There has currently been considerable interest in the structural, electronic, and optical properties of the transition-metal dichalcogenides and their intercalation compounds.<sup>1,2</sup> These compounds have the formula  $\text{MX}_2$  ( $X=\text{S,Se}$ ;  $M=\text{Ti,Zr,Hf,V,Nb,Ta,Mo,W}$ ). They are highly anisotropic solids and they can be intercalated by various electron donors or Lewis bases such as alkali metals and many organic molecules between the layers.<sup>1-3</sup>

Detailed studies on the electronic structure of  $\text{TiS}_2$ , however, have produced conflicting conclusions.<sup>4-19</sup> On one hand, some band-structure calculations<sup>9</sup> conclude to an indirect  $p/d$  band overlap ranging from 0.2 to 1.5 eV. Others instead tend to prove that  $\text{TiS}_2$  is a narrow-gap semiconductor. The experimental evidence gathered in photoemission have been interpreted as indicating either a semimetallic (Williams and Sheperd<sup>9b</sup>) or a semiconducting (Chen *et al.*<sup>9a</sup>) behavior. Moreover, resistivity measurements in the highly stoichiometric titanium disulfide show at all temperatures metallic behavior.<sup>19</sup>

In order to bring new arguments into this discussion, we present in this paper both experimental and theoretical analyses on S  $K$ -edge x-ray-absorption near-edge structure (XANES) and Ti  $L_{2,3}$ -edge electron-loss near-edge structure (ELNES) spectra. As is well known, these spectroscopies provide direct information not only on the structural arrange-

ment around a selected atomic species but also on the local electronic structure.<sup>20,21</sup>

$\text{TiS}_2$  has been prepared as described in Ref. 22 and is as stoichiometric as possible, even if a slight excess of titanium in the van der Waals gap cannot be avoided (less than  $2 \times 10^{-3}$ ).<sup>22</sup> In order to prevent degradation, samples were handled in glove boxes and transferred to the different systems for analysis via appropriate air-tight containers.

The electron-energy-loss spectroscopy experiments (titanium  $L_{2,3}$ -edges) have been carried out on a CM30 Philips transmission electron microscope, operated at 200 kV and equipped with a Gatan 666 multichannel spectrometer. The experimental conditions led to an energy resolution of 0.9 eV full width at half maximum for the zero loss peak. XANES spectra were recorded using the French synchrotron radiation source at LURE (Orsay). The sulfur  $K$  edge was recorded on the Super ACO storage ring, with a Si(111) two-crystal monochromator, and 0.4 eV resolution.

All our calculations of the XANES spectra are based on the one-electron multiple-scattering (MS) theory of Lee and Pendry,<sup>23</sup> as implemented and developed by several authors.<sup>21,23-28</sup> In this theory the absorption coefficient is proportional to a smoothly varying atomic dipole transition matrix element times a factor describing the local projected density of states at the energy of the excited photoelectron. It

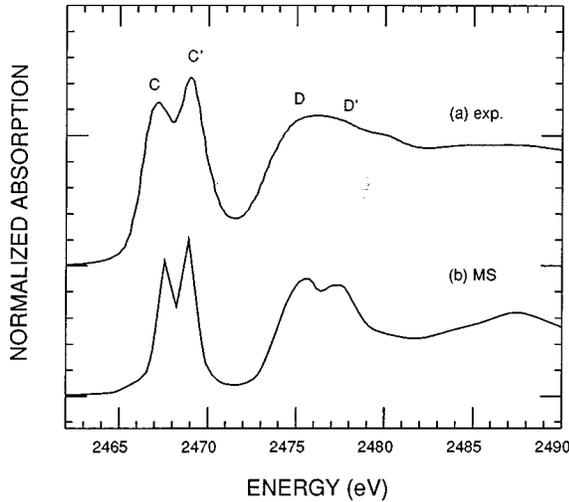


FIG. 1. (a) The experimental S *K*-edge XANES spectrum for TiS<sub>2</sub> compound. The transitions of  $1s \rightarrow 3d^1(t_{2g})\underline{L}$  and  $1s \rightarrow 3d^1(e_g)\underline{L}$  (sulfur  $3p$ -titanium  $3d$  antibonding states) are indicated by *C* and *C'*, respectively. (b) MS calculation of the sulfur *K*-edge spectrum. The “twin peak” is well reproduced.

is a fact that MS theory has been widely and successfully used to interpret and determine the local geometrical and electronic structure properties of many systems, especially for the metallic and covalent ones.<sup>21,23-31</sup>

We use Mattheiss’s prescription<sup>32</sup> to construct the cluster density and we obtain the Coulomb part of the potential by superposition of neutral atomic charge densities using Clementi and Roetti tables.<sup>33</sup> In order to simulate the charge relaxation around the core hole, we use the well-screened  $Z+1$  approximation (final-state rule).<sup>34</sup> For the exchange-correlation part of the potential we use the energy- and position-dependent complex Hedin-Lundquist (H-L) self-energy  $\Sigma(\vec{r}, E)$ .<sup>35</sup> The calculated spectra are further convoluted with a Lorentzian-shaped function with a full width  $\Gamma_h \approx 0.59$  eV for the S *K* edge and 0.1 eV for the Ti  $L_{2,3}$  edge<sup>36,37</sup> to account for the core hole lifetime. We have chosen the muffin-tin radii according to the criterion of Norman,<sup>38</sup> and allowed a 10% overlap between contiguous spheres to simulate the atomic bond.

In Fig. 1 we present the experimental sulfur *K*-edge absorption spectra of TiS<sub>2</sub> (curve a) which is comparable to previous results<sup>12</sup> with improved experimental resolution. Since the first electron-addition states in TiS<sub>2</sub> are Ti  $3d$  states<sup>39</sup> antibonding with S  $3p$  orbitals, the first two peaks labeled *C* and *C'* observed in the S *K* edge are identified as being these states, which can be assigned approximately to transitions to  $t_{2g}$  and  $e_g$  bandlike states. Their energy separation ( $t_{2g} - e_g$  splitting) is about 2.0(1) eV and agrees with that found by Fischer<sup>7</sup> and other studies based on a molecular-orbital treatment.<sup>12,16,40-48</sup> Following the authors of Ref. [39], in a configuration interaction (CI) approach these peaks get their transition probability from the hybridization of the ground state.<sup>39,44</sup> In fact, in a cluster with Ti in an octahedron of S ions, the ground state is well described by the admixture of configurations

$$\Phi_G = \alpha |t_{2g}^1 \underline{L}\rangle + \beta |e_g^1 \underline{L}\rangle + \gamma |3d^0\rangle, \quad (1)$$

where  $L$  denotes a hole in ligand sulfur. The first two terms in the right-hand side of Eq. (1) are ligand-metal charge-transfer low-energy hybridization states (or antibonding levels in molecular-orbital theory): due to covalency the  $d^0$  state mixes with states in which an electron has jumped from the ligand to titanium  $3d$  orbitals and in a first approximation the transition probability to states of  $t_{2g}$  and  $e_g$  symmetry is proportional to  $\alpha^2$  and  $\beta^2$ , respectively. These states are probed in the Ti  $L_{2,3}$  edges and S *K*-edge ELNES/XANES spectra. Clearly, in the solid these levels broaden into two narrow bands. Moreover, it is well known that a connection can be established between the band picture and the CI approach. It is sufficient to perform a unitary transformation on the occupied Bloch states in the Slater determinant representing the uncorrelated ground-state wave function to Wannier states, thereby obtaining a description of the extended system in terms of localized orbitals and ultimately Oxin terms of occupancy of atomic orbitals on atomic sites. This latter description is the same as that used in the CI picture. The only difference in the two approaches is the value of the admixture coefficients in Eq. (1), which control the amplitude probabilities in the absorption measurements.

Returning to our spectrum, the peaks *D* and *D'*, at about 10 eV above threshold, reflect a  $p$ -type projected density of states due to metal  $4s$  and  $4p$  states hybridized with sulfur  $3p$  states, of approximately  $t_{1u}$  symmetry.<sup>44</sup>

The curve *b* in Fig. 1 is a MS calculation of a S *K*-edge XANES spectrum. Calculations were carried out on atomic clusters containing increasing numbers of atoms up to the eighth shell, until convergence was reached. The final cluster has  $C_{3v}$  symmetry<sup>49</sup> and includes 81 atoms within 7.0 Å from the central sulfur atom. The two main prepeaks, which have been clarified as arising from  $1s \rightarrow |t_{2g}^1 \underline{L}\rangle$  and  $1s \rightarrow |e_g^1 \underline{L}\rangle$  transitions, and the features in MS region are very well reproduced both in relative amplitude and energy position. The fact that a simple MS approach, based on a one-electron picture in an effective potential, is capable of giving such a good agreement with the S *K*-edge absorption spectrum, is already an indication that the admixture coefficients in Eq. (1) are those relative to the band picture.

In order to verify this conclusion we have examined the Ti  $L_{2,3}$  absorption edges, which are very sensitive to interatomic electron correlation effects. It is a well-known fact indeed that in a transition-metal compound the  $2p$  hole in the final state can couple with the localized  $3d$  excited electron to give rise to a multiplet structure, due to interatomic correlations, which manifests itself in the absorption spectra. In Fig. 2 we show both the experimental ELNES spectrum and the theoretical calculation of Ti  $L_{2,3}$  edges. The most obvious feature of the experimental  $L_{2,3}$  spectrum is the spin-orbit splitting of the  $2p_{3/2}$  and  $2p_{1/2}$  lines: this is about 5.75 eV, roughly the same as in the case of TiO<sub>2</sub> (5.44 eV).<sup>45</sup> Furthermore, the  $L_3$  and  $L_2$  lines are split in two peaks with about 2.0(2) eV energy separation. This is attributed to the crystal-field splitting of the  $t_{2g}$  and  $e_g$  orbitals as mentioned above. Apparently, no other feature is present that could be related to as arising from multiplet structure. This is at variance with the TiO<sub>2</sub> case,<sup>45</sup> where a three-peak structure is observed, and shows that TiS<sub>2</sub> is a weak-electron-correlated system. The theoretical calculation reproduces this behavior as

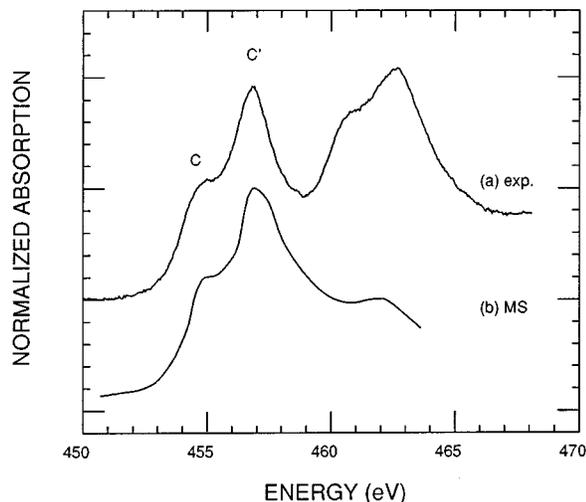


FIG. 2. (a) Experimental ELNES spectrum at Ti  $L_{2,3}$  edges for  $\text{TiS}_2$  compound. Peaks  $C$  and  $C'$  correspond to transitions of  $2p$  to  $t_{2g}$  and  $e_g$ , respectively. (b) MS computation of total cross-section. The “twin peak” is well reproduced.

shown by curve  $b$  in Fig. 2. Since in our theory the absorption coefficient is nearly independent from the initial spin-orbit split edge we only show the result for the  $L_3$  edge.

Moreover, we observe that the intensity of the first peak corresponding to transition to  $t_{2g}$  bandlike state in both S  $K$ -edge XANES and Ti  $L_{2,3}$ -edge ELNES spectra is lower than the second one, quite at variance once again with the case of  $\text{TiO}_2$ ,<sup>44,45</sup> where the amplitudes of the two peaks are almost identical both in O  $K$ -edge and Ti  $L_{2,3}$ -edge spectra and interatomic correlations are clearly present.<sup>45</sup> It is difficult to justify such low intensities for the first peaks as compared to that of the second ones in  $\text{TiS}_2$  by a simple covalency effect as it was used to explain the complementarity between the  $L_{2,3}$  edge of a transition metal and the O  $K$ -edge peak intensities in some manganese and titanium oxides.<sup>50</sup> As demonstrated above, a bandlike approach seems to be more appropriate for the description of the experimental observations. This is especially valuable for the  $\text{TiS}_2$  in

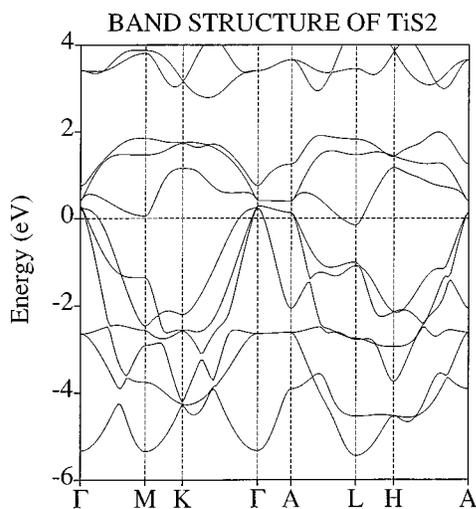


FIG. 3. Energy band structure of  $\text{TiS}_2$ .

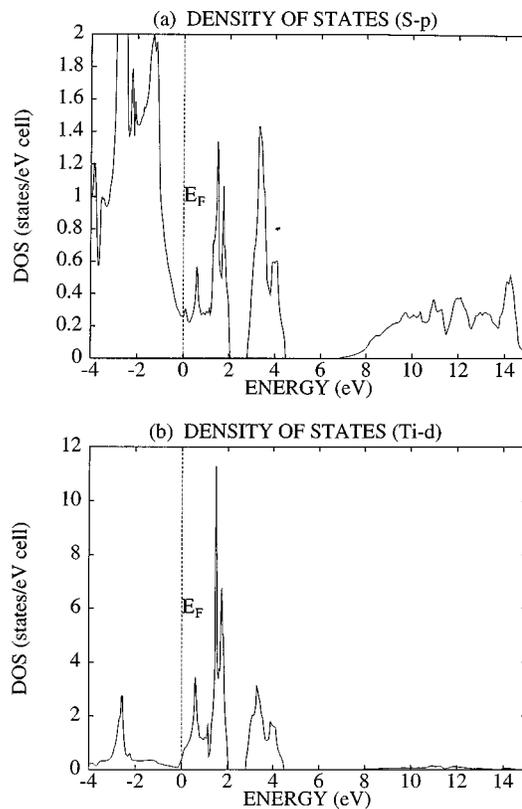


FIG. 4. (a) S  $p$ -projected density of states and (b) Ti  $d$ -projected density of states of  $\text{TiS}_2$  as derived from the LMTO band-structure calculation.

which Ti has a  $d^0$  configuration in an octahedral symmetry. In order to gain further insight into the electronic structure of  $\text{TiS}_2$  we have performed tight-binding linear muffin-tin orbital (TB-LMTO) band-structure calculations,<sup>51–53</sup> which are presented in Fig. 3 and are very similar to linear augmented-plane-wave (LAPW) ones.<sup>54</sup> We obtain from the band structure an indirect overlap of about 0.4 eV between the top of the valence band and the bottom of the conduction band. This overlap could affect strongly the hybridized lowest S  $3p$  and Ti  $3d$  states, since if one electron occupies  $t_{2g}$  band, then the final state corresponding to the transition  $1s \rightarrow |t_{2g}^1 L$  in Eq. (1) will involve two  $3d$  electrons. From a CI point of view, this is an argument that can explain why the intensity of the first peak in both S  $K$ -edge and Ti  $L_{2,3}$ -edge spectra is lower than the second one. In a bandlike one-electron picture the effect comes out automatically from the calculated DOS.

In order to make contact with MS calculations, we present in Fig. 4 the  $p$ -projected density of states (DOS) of sulfur [panel (a)] and  $d$ -projected DOS of titanium [panel (b)]. Taking into account that effects of the matrix elements are not included, reasonable agreement is achieved with MS cluster calculation: there are two peaks in the first region above the Fermi level ( $E_f$ ) in the  $p$ -projected DOS that correspond to peaks  $C$  and  $C'$  in the S  $K$  edge; similar agreement is observed between the DOS structure at about 8.5–14 eV and features  $D$  and  $D'$  at the same edge.

Our theoretical calculations performed for a perfectly stoichiometric compound fit rather well the experimental data

indicating that off stoichiometry does not affect significantly our compounds. In fact, excess of Ti atoms would have favored the appearance of correlation effects in the absorption spectra, due to dangling  $3d$  atomic orbitals.

All the evidence coming from the preceding arguments—the absence of multiplet structures in the Ti  $L_{2,3}$  edge, the striking difference of the  $C$  and  $C'$  peak intensity, and the calculated DOS, which has been shown to be very appropriate in this case and does not go to zero near  $E_f$ —indicate that  $\text{TiS}_2$  is a semimetal.

In conclusion, we have been able to interpret the S  $K$ -edge XANES and Ti  $L_{2,3}$ -edge ELNES spectra in terms of a one-electron picture. This fact, together with experimental indications about the purity of our samples and the results of our TB-LMTO band-structure calculations, places the  $\text{TiS}_2$

system on the semimetal side of the Zaanen, Sawatzky, and Allen diagram,<sup>57</sup> as predicted by these authors. In this first paper, we have demonstrated that the combination of XANES and ELNES spectroscopies, MS simulations, and band-structure calculations is a very powerful tool in understanding the behavior of lamellar transition-metal dichalcogenides. Similar studies are in progress to investigate  $\text{TiS}_2$  parent phases and intercalation process.

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