

Sulfur *K*-Edge X-Ray-Absorption Study of the Charge Transfer upon Lithium Intercalation into Titanium Disulfide

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Sulfur *K*-edge x-ray-absorption spectra have been recorded for lithium intercalated titanium disulfides Li_xTiS_2 . The near-edge features up to 30 eV above threshold are interpreted in the framework of full multiple-scattering theory. We show that the electrons transferred from intercalated lithium atoms are not only located on Ti *3d* orbitals, as previously assumed, but also on the S *3p* states. For comparison, we present the S *p*-projected density of states derived from linear muffin-tin-orbital band structure calculations. An overall agreement between measurement and theory is very well achieved. [S0031-9007(96)00962-3]

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Lamellar transition metal dichalcogenides (TMDC) MX_2 ($X = \text{S, Se}; M = \text{Ti, Zr, Hf, V, Nb, Ta, Mo, or W}$) have been among the first phases considered as a host in intercalation reaction in which a guest species, atom, ion, or molecule can be reversibly inserted into empty spaces of the host structure [1–4]. Until quite recently, it has been thought that the guest species provides an electron to the transition metal (TM) *d* orbitals [5–8]. Such a conclusion is mainly based on a rigid band model. More recent investigations [9,10] tend to show that this model is not adequate to study the intercalation process. Moreover electronic band structure calculations [11] in the extended Hückel approach have shown that, in the case of lithium intercalation into titanium disulfide TiS_2 , there exists a partial electronic transfer of lithium *2s* electron to the host structure, on both titanium and sulfur atoms. However, such an approach remains qualitative and is not able to explain the edge shape changes, especially in separating structural and electronic effects. To do so, it is necessary to combine accurate electronic band structure calculations and edge simulations. In this Letter, we present new x-ray absorption spectroscopy (XAS) data and theoretical analyses on the Li intercalated compound TiS_2 that demonstrate the important role of sulfur atoms and provide a correct picture in the intercalation process on TMDC.

TiS_2 has been prepared as described in Ref. [12]. Lithium intercalation has been performed by the *n*-butyl lithium technique at room temperature [13] with the lithium content determined by flame spectroscopy. In order to prevent degradation, samples were handled in glove boxes and transferred to the different systems for analysis via appropriate airtight containers. X-ray appearance near-edge structure (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 Si111 two-crystal monochromator, with a 0.4 eV resolution.

All the computations of the XANES spectra were carried out using the multiple-scattering CONTINUUM code [14] based on the one-electron full multiple-scattering (MS) theory [15–17]. The cluster potential was approximated by a set of spherically averaged muffin-tin (MT) potential, which was built by following the standard Mattheiss prescription [18]: atomic charge densities obtained from self-consistent solutions of the Dirac equations were placed on each atomic site in the cluster, and the superposed charge density was spherically averaged in spheres around the atom whose potential was required. The Coulomb part of each atomic potential was generated using charge densities of neutral atoms obtained from Clementi and Roetti atomic wave function tables [19]. Then the Poisson's equation for the Coulomb or Hartree part of the potential was solved, and an appropriate exchange and correlation potential [e.g., the X_α or the energy- and position-dependent complex Hedin-Lundquist (HL) self-energy $\Sigma(\vec{r}, E)$] was added. We refer the reader to Refs. [20,21] and references therein for a detailed discussion. In order to simulate the charge relaxation around the core hole in the photoabsorber of atomic number Z (16 in the case of S), we use the well screened $Z + 1$ approximation (final state rule) [16]. This consists in taking the orbitals of the $Z + 1$ atom and constructing the charge density by using the excited electronic configuration of the photoabsorber with the core electron promoted to an empty orbital. We have chosen the muffin-tin radii according to the criterion of Norman [22], and allowed a 10% overlap between contiguous spheres to simulate the atomic bond. The calculated spectra are further convoluted with a Lorentzian shaped function with a full width $\Gamma_h \approx 0.59$ eV for S *K* edge [23] to account for the core hole lifetime and $\Gamma_{\text{exp}} \approx 0.40$ eV for experimental resolution.

Density of states calculations were performed by using the local density approximation and the tight-binding muffin-tin orbital method in the atomic sphere approximation (TB-LMTO-ASA) [24,25].

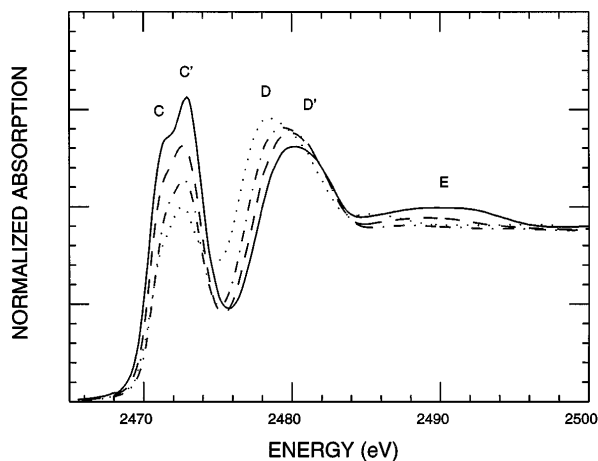


FIG. 1. Experimental XANES spectra at S *K* edge for TiS_2 (solid line), $\text{Li}_{0.4}\text{TiS}_2$ (dashed line), $\text{Li}_{0.8}\text{TiS}_2$ (dash-dotted line), and Li_1TiS_2 (dotted line).

Figure 1 shows the experimental sulfur *K* edge XANES spectra of Li_xTiS_2 for x between 0.0 and 1.0 after background subtraction and normalization. Two main features can be observed, each one corresponding to two poorly resolved peaks as previously shown [26]. They have been labeled *C*, *C'*, *D*, and *D'*. Since the first electron-addition states are Ti *3d* states [27] antibonding with S *3p* orbitals, the first double peaks *C* and *C'* observed in the S *K* edge have been identified as these states, which can be assigned approximately to transitions to t_{2g} and e_g bandlike states. This assignment agrees with the one of Fischer and other studies based on a molecular-orbital treatment [28–30]. de Groot *et al.* [31] have analyzed in detail the recorded spectral features of some *3d* TM oxides in terms of ligand-field theory. The energy separation between *C* and *C'* peaks (t_{2g} - e_g splitting) is about 2.0 eV which is approximately equal to that obtained by Fischer [28] (2.1 eV), Ohno *et al.* [29] (2.0 eV), and Sugiura *et al.* [32] (2.0 eV).

Upon lithium intercalation the intensity and width of prepeaks *C* and *C'* decrease but no noticeable energy shift is observed. Peak *C* seems to be more influenced by the intercalation than *C'*. The next peaks *D* and *D'* at about 8 eV above the *C* feature reflect a *p*-type projected density of states. In this part, the sulfur *3p* orbitals are hybridized with the Ti *4s* and *4p* bands and constitutes a kind of accessible continuum state. We note that there are two interesting trends for these double peaks upon lithium intercalation: a progressive shift toward lower energy and an increase of the intensity. Another small feature *E* can be seen about 20 eV above the *C* peak. Its intensity decreases upon lithium intercalation, and it seems to be shifted towards lower energy.

In a preceding paper [26] the edge shape of the pristine material has been nicely analyzed by full MS theory calculations. It has been shown that the peaks *C* and *C'* can be described by taking into account a ground state made of the admixture of configurations

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

where \bar{L} denotes a hole in ligand sulfur. The first two terms in the right-hand side of Eq. (1) correspond to the ligand-metal charge-transfer low-energy hybridization states, or in other words, to a part of the sulfur-titanium bond. This can be used to explain the changes in the S *K* edge upon lithium intercalation process.

In Fig. 2 we present MS calculations of the S *K* edge XANES spectra for Li_1TiS_2 by using different cluster sizes around the excited atom. Li_1TiS_2 has the same structure as the host TiS_2 but with different lattice constants $a_0 = 3.459 \text{ \AA}$ and $c_0 = 6.188 \text{ \AA}$ [33], larger than the TiS_2 ones ($a_0 = 3.406 \text{ \AA}$, $c_0 = 5.694 \text{ \AA}$) [12]. For S the central atom, the first shell consists of three Ti and three Li atoms, instead of only three Ti in the TiS_2 compound. The peak *C* is reproduced by using solely the first three Ti atoms. Hence this feature reflects transitions to *3p* states hybridized with the narrow metal *3d* band. The double structures are only reproduced in the larger cluster calculations, indicating that one would need to take into account higher coordination neighbors in constructing molecular orbitals, e.g., t_{2g} and e_g in octahedral symmetry. This just explains why some lower energy features are sensitive to so-called “long-range” effects. The seven atom cluster (including the first three Li atoms) already gives rise to a relatively sharp peak and a small part contribution to feature *D'*. After adding the first S shell as shown by the 19-atom cluster calculation, the peak *D'* is very well defined. This feature reflects transitions to sulfur *3p* states hybridized with Ti delocalized *4s* and *4p* states [31]. This demonstrates the influence of the relatively strong

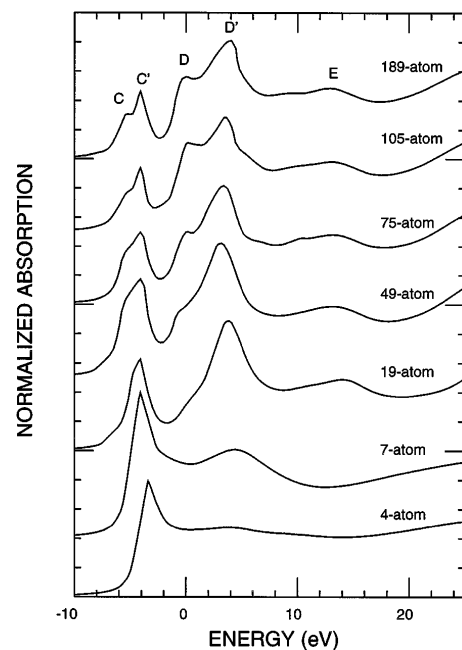


FIG. 2. MS calculation of the sulfur *K*-edge XANES spectra in Li_1TiS_2 for different atomic clusters.

backscattering of the S^{2-} ion and can be understood as a caging effect of the S shell on the excited electron: the backscattering creates a relatively sharp scattering resonance around the absorber atom. This is in agreement with the findings of Vvedensky and Pendry [34] on NiO, Lindner *et al.* [35] and Rez *et al.* [36] on MgO, and Kurata *et al.* on MnO [37]. Peak *E* is also reproduced within this cluster indicating that this feature arises from dominantly single-scattering events from this first S shell, as suggested by the simple resonance scattering arguments. The structure *D* appears after adding several shell atoms and its intensity increases with the increasing of cluster size until 105-atom cluster calculation, showing that the final state reached in the core electron transition is not a simple atomic or molecular state [38].

A simple comparison between the calculated sulfur *K* edges for TiS_2 and Li_1TiS_2 in Fig. 3 shows that the MS calculations are able to reproduce the variation of relative intensities and shift of peaks *C*, *C'*, *D*, and *D'*. The intensity of the peak in the spectrum is related to the degree of hybridization of the considered atom. In the case of lithium intercalation there are three parameters which may change the sulfur hybridization. Increasing the sulfur coordination number from three in TiS_2 to six in Li_1TiS_2 (with the same bond lengths of S-Ti and S-Li) would increase the hybridization. At the same time the Ti-S bond length increases from 2.428 to 2.473 Å [39], and this will reduce the hybridization between titanium and sulfur. Finally the hybridization in the ground state between S $3p$ and Ti $3d$ will decrease with *x* since if titanium has an electron transferred in the t_{2g} level from donor Li, then the first term in Eq. (1) will involve two electrons which will be higher in energy by the Coulomb interaction U_{dd} . It is impossible to experimentally separate the different contributions. To do it, we have performed MS calculations on the last cluster model with the same cell and structural parameters of

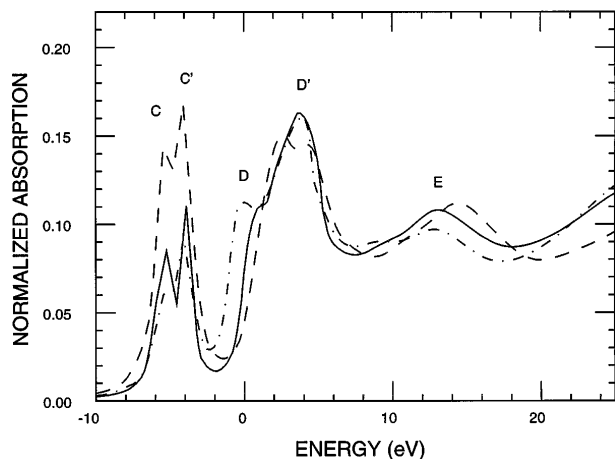


FIG. 3. MS calculation of the sulfur *K*-edge XANES spectra in TiS_2 (dashed line), Li_1TiS_2 (dash-dotted line), and, for comparison, pseudocompound (see text) Li_0TiS_2 (solid line).

Li_1TiS_2 , but without lithium inside the van der Waals gap. We refer to this pseudocompound as “ Li_0TiS_2 .” Such a hypothetical compound takes into account the structural effects but neither the change in the coordination number nor the charge transfer from lithium to the host. The results have been compared to those of TiS_2 and Li_1TiS_2 as shown with the solid line. The important decrease of the *C* and *C'* peaks is quite similar in Li_1TiS_2 and Li_0TiS_2 , proving that the main influence in the preedge is the elongation of the titanium-sulfur bond. Nevertheless it is clear in the simulations that the *C* peak is weaker in the Li_1TiS_2 than in Li_0TiS_2 . This can be attributed to the partial filling of the t_{2g} levels by the electron transferred from the lithium atom, reducing the probability of S $1s$ electron transition to these levels in the absorption process. On the contrary, the intensity and position of the *D* and *D'* peaks are almost not changed by the only structural modifications. The occurrence of a new feature at lower energies, in good agreement with the shift and the increase observed in the experimental spectra, is obtained only if lithium is really taken into account in the calculations. It proves that, this time, the effect is mainly due to the charge transfer between lithium and sulfur atoms and the change in the sulfur coordination number.

The evidence of such a change has to be found in a modification of the band structure. For this purpose a new band structure has been performed, by using the TB-LMTO-ASA method, and the projected densities of states (DOS) on the sulfur *p* orbitals are presented in Fig. 4. The origin of the energy scale has been arbitrarily fixed at the Fermi level E_f . Just above it we may find the doublet

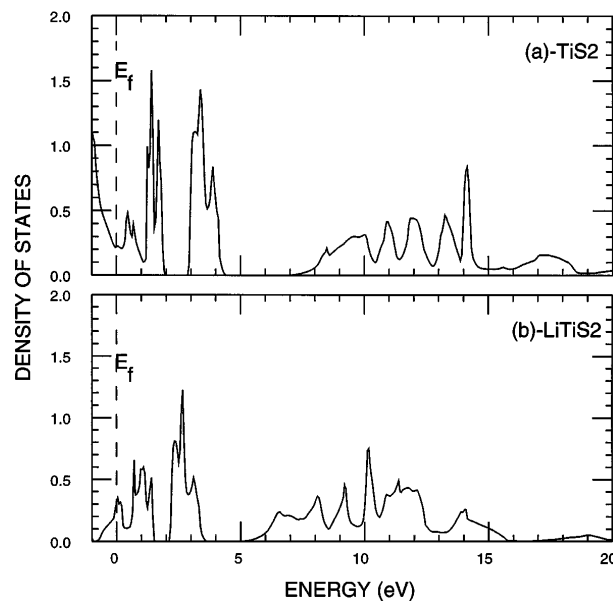


FIG. 4. Linear muffin-tin orbital (LMTO) band structure calculations: (a) S *p*-projected density of states for TiS_2 ; (b) S *p*-projected density of states for Li_1TiS_2 . The origin of the energy scale has been arbitrarily fixed at the Fermi level E_f .

corresponding to sulfur p states mixed with the titanium t_{2g} and e_g levels. Upon intercalation, E_f readily moves into the t_{2g} band which narrows and becomes lower in intensity. We may also notice that the energy difference between E_f and the end of the e_g peak decreases from 4.2 to 3.5 eV, in good agreement with the $C-C'$ feature narrowing observed in Fig. 1, of about 1.0 eV. A large shift of about 2 eV towards lower energy is observed for the second part related to features D and D' . Such a shift explains well the above-mentioned experimental shift of 1.7 eV. It is worthwhile mentioning that this shift allows a nice matching between empty sulfur $3p$ states and lithium $2s$ states, indicating a noticeable lithium sulfur interaction.

By an appropriate combination of MS and band structure calculations, we have then been able to explain the various changes in the sulfur K edge of the TiS_2 upon lithium intercalation. The important modifications of the prepeak intensities can be largely explained by the structural changes and the partial filling of the titanium t_{2g} levels. The shifts and broadening of features D and D' are more influenced by the change of coordination number and S-Li interaction, i.e., the charge transfer. These new results definitely prove that sulfur is largely taking part in the intercalation process. Similar studies are currently under way on parent compounds, in changing either the host or the guest species.

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