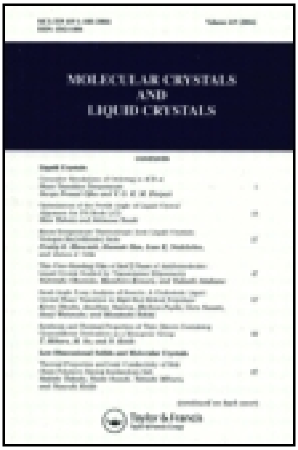

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A Unique Tool to Study the Intercalation Process

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XAFS: A Unique Tool to Study the Intercalation Process

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We applied X-ray Absorption Spectroscopy, in combination with electronic band structure calculations, to probe the electronic structure before and after lithium intercalation into TiS_2, $TiSe_2$ and 2H-$NbSe_2$. We are then able to precisely determine the nature of the charge transfer from intercalated lithium to the host. It is shown that lithium is not fully ionized and that chalcogen atoms are deeply involved in the charge transfer process.

Keywords: lithium intercalation; lamellar dichalcogenides; charge transfer; electronic structure; x-ray absorption

INTRODUCTION

Lithium batteries, using intercalation process, appear to be one of the more promising way to store energy. In order to understand their behaviour it is of primary importance to precise the nature of the charge transfer upon intercalation. Up to a recent past, it has been generally considered that lithium intercalation into transition metal compounds proceeds via a complete ionization of lithium and the consecutive transfer of one electron to the host structure, essentially on the transition metal d orbitals[1]. Such a conclusion is essentially based on the so-called "rigid band model" which supposes that the electronic band structure is not modified by intercalation. Nevertheless, some careful band structure calculations performed on the actual atomic structures before and after intercalation, i.e. far from the rigid band model, conclude to a partial ionization of lithium atoms and a charge transfer which does not concern only the transition metal d levels but also the chalcogen electronic levels[2,3]. The only way to precisely characterize the charge transfer consists in the determination of the number of transferred electrons, on which atom of the host structure and, if possible, on which orbitals of these atoms. This can be only done by electronic band structure calculations but, due to the fact that these methods always contain some approximations, it is of primary importance to ascert their results by experimental techniques able to probe the occupied or empty electronic levels of the band structure.

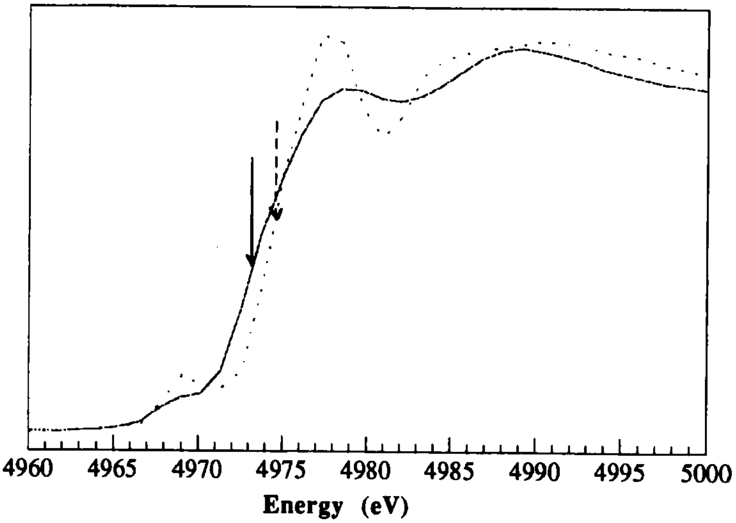

FIGURE 1: Titanium K edge in $TiSe_2$ (dots) and Li_1TiSe_2 (full line). The arrows indicate the positions of the main edges.

X-ray absorption spectroscopy (XAS) is very well adapted for such a probing, being a bulk technique, easily performed on air sensitive compounds, and highly selective in atoms and orbitals, in choosing a given edge by an appropriate energy range. We will demonstrate how this technique is especially suited to probe the electronic structure and then characterize the charge transfer upon lithium intercalation into lamellar transition metal dichalcogenides. Edge simulations are also able to comfort the conclusions, being a direct transposition of calculated electronic structures in the direct space, taking into account the interaction matrix between the electronic levels in the transition. This will be illustrated on TiS_2, $TiSe_2$ and 2H-$NbSe_2$.

EXPERIMENTAL

The host materials have been synthesized in the classical high temperature way and lithium intercalation has been performed by the n-butyl lithium technique. XAS data have been collected at LURE, the French synchrotron radiation facility, on the DCI storage ring for high energy edges and on the on the Super-ACO one for lower energies.

Band structure calculations have been performed by using two different ab-initio DFT methods: the TB-LMTO-ASA[4] and the FLAPW in the WIEN 95 code[5]. Edge simulations use a multiple scattering approach with the CONTINUUM code[6].

LITHIUM-TiX_2 (X=S, Se)

We present together the results on these two host structures because their atomic structures and therefore their electronic band structures are very similar. Accurate calculations have been performed in the TB-LMTO-ASA formalism. They confirm the classical view of the first empty electronic levels, i.e. the splitting in the so-called "t_{2g}" and "e_g" levels due to the octahedral coordination of titanium atoms. Nevertheless, it is important to note that these levels are not only titanium d orbitals. They also contain noticeable contributions of chalcogen p orbitals (about 25%) and even titanium p and chalcogen d orbitals. This means that due its high selectivity, XAS will be able to probe the filling of these electronic levels whatever the considered edge. In effect all the changes in the edge shapes can be perfectly explained with the projected density of states (DOS)[7]. Figure 1 represents the changes in the titanium K edge upon lithium intercalation into $TiSe_2$. It is made of small prepeaks (around 4970 eV) and a main edge. The prepeaks correspond to the titanium p levels inside the t_{2g} and e_g groups. We observe a decrease of the prepeaks and a shift of about 1.5 eV of the main edge, when lithium is intercalated. The same behaviour, with various amplitudes, is observed on the chalcogen K edge. The decrease of the prepeaks is mainly due to the slight structure modifications upon intercalation, as demonstrated for the sulfur K edge in the TiS_2 case[7]. The main edge shift corresponds to the general displacement of the DOS in this part of the electronic structure, in relation with the reduction of both titanium and chalcogen atoms. In the selenium L3 edge, the intensity of the prepeaks increases with the lithium content, as we will observe for the niobium diselenide.

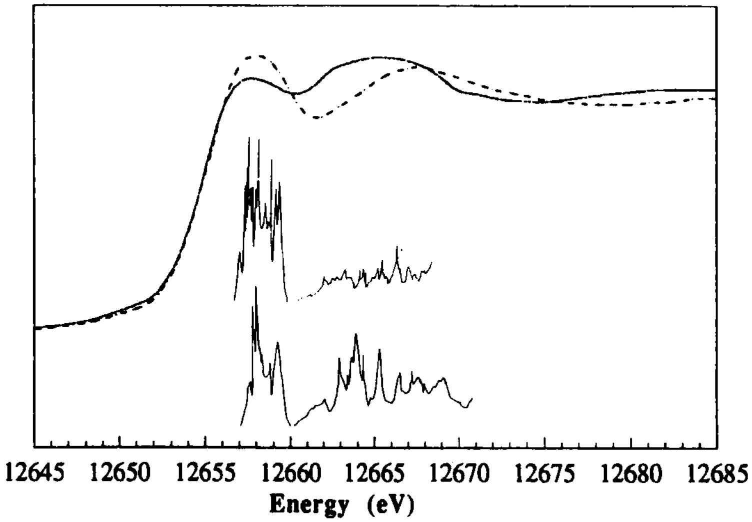

FIGURE 2: Selenium K edge in $NbSe_2$ (dots) and Li_1NbSe_2 (full line) compared with the respective DOS projected on the selenium p orbitals (above: $NbSe_2$ and below: Li_1NbSe_2).

From the so nicely probed calculated electronic structures, it is possible to estimate the charge transfer. It can be calculated, in the case of TiS_2, that lithium is not fully ionized and that the 0.78 transferred electrons are almost exactly shared by sulfur (0.27 electron per sulfur) and titanium (0.24 electron) atom. Moreover the lithium-chalcogen interactions in the intercalated phase are certainly not negligible.

LITHIUM-NbSe$_2$

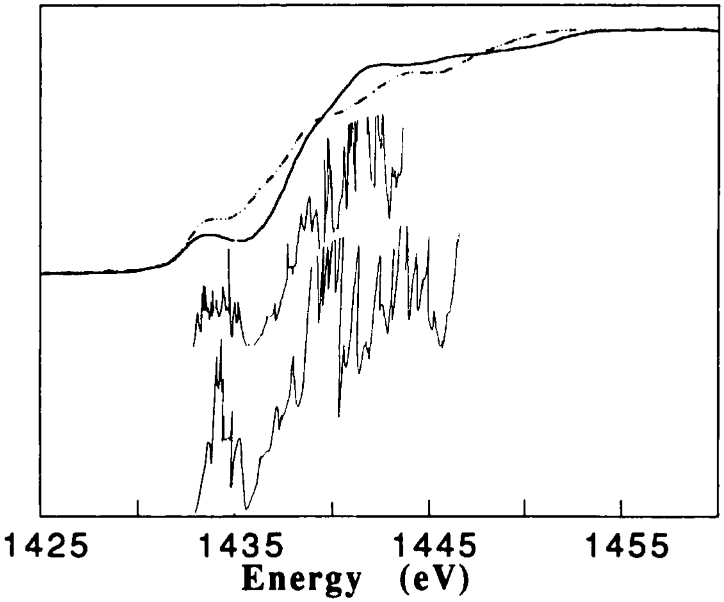

FIGURE 3: Selenium L3 edge in $NbSe_2$ (full line) and Li_1NbSe_2 (dots) compared with the respective DOS projected on the selenium d orbitals (above: $NbSe_2$ and below: Li_1NbSe_2).

As compared to the previous examples, this case is especially interesting due to the trigonal prismatic coordination of niobium and the easy access by XAS to the transition metal L edges. It is then possible to probe directly its electronic d levels which are the main part of the DOS just above the Fermi level. Band structures have been calculated within the FLAPW formalism. As expected for the niobium in a trigonal prismatic coordination of selenium atoms, the valence band is splitted into two main parts in the first 5 eV. The first one is called A' in the D_{3h} group and is half filled by electrons, in agreement with the metallic behaviour. The second large part is made of E' and E" orbitals. It is interesting to note that, if these orbitals are largely niobium d ones, the selenium p ones contribute to the total DOS for about 20% with the same shape. Even the niobium p orbitals and selenium d orbitals reflect exactly this common shape despite their very low contributions of about 1 and 2 percents of the total DOS.

As previously observed for the titanium derivatives, XAS is able to confirm these calculations. Figure 2 compares the selenium K edge of $NbSe_2$ and $LiNbSe_2$ with the calculated DOS projected on the selenium p orbitals. A very good agreement is observed between the experimental data and the calculations in both position and intensities of the different singularities. The same is true for the selenium L3 edge and the DOS projected on the selenium d orbitals (Figure 3). It is interesting to note that, as previously seen in the $TiSe_2$ case, that the contribution of the selenium d levels in the first empty states increases upon lithium intercalation while it decreases for the selenium p ones . This is likely the signature of the small but significant changes in the NbSe6 trigonal prism geometry and then the orbital overlapping.

Once more, these changes in the selenium edges prove that chalcogen is largely taking part in the intercalation and the charge transfer process. Large modifications are also observed on the niobium L3 edges but, this time, the calculated DOS fail to explain the occurrence of an extra peak at higher energy when lithium is intercalated. Nevertheless, edge simulations are able to reproduce precisely the changes and have proved that the new peak comes from interactions with lithium atoms and multiple scattering effects..

Acknowledgements

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