

## Molecular modelling of lithium intercalation in $1T - \text{TiS}_2$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 3011

(<http://iopscience.iop.org/0953-8984/9/14/015>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 08:27

Please note that [terms and conditions apply](#).

## Molecular modelling of lithium intercalation in 1T-TiS<sub>2</sub>

Fernando Mendizábal<sup>†</sup>, Renato Contreras<sup>†</sup> and Arie Aizman<sup>‡</sup>

<sup>†</sup> Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

<sup>‡</sup> Departamento de Química, Universidad Técnica Federico Santa María, Casilla 110-V, Valparaiso, Chile

Received 12 June 1996, in final form 22 November 1996

**Abstract.** The electronic structure of 1T-TiS<sub>2</sub> intercalated with lithium is analysed within a molecular approach that uses a finite-size cluster to represent the solid. Electronic descriptors such as the electronic chemical potential, bond order and the density of states are used to discuss the bonding properties and migration of lithium within the layered lattice. A detailed analysis of the electronic structure reveals the major role of local interactions involved in the electronic polarization of the impurity's environment. The results compare well with the available experimental data.

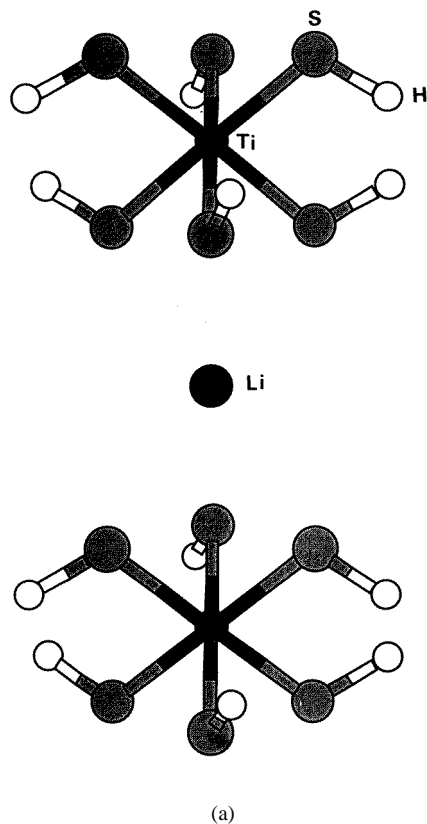
### 1. Introduction

Transition metal dichalcogenides are classified as bidimensional solids presenting a layered structure [1, 2]. The layers are bound by weak Van der Waals interactions, so an interlaminar space (the Van der Waals (VDW) gap) is available in which to intercalate atoms and molecules [3, 4]. The intercalation process is in general associated with a charge transfer that involves the atomic or molecular orbitals of the impurity and the bands of the solids [5]. In the particular case of the transition metal dichalcogenides (MX<sub>2</sub>) series, the guest transfers an amount of electronic charge to the conduction band (CB) of the solid, thereby leaving a positive ion in the VDW gap. If the intercalated species are alkali or metal atoms, their reactions may be described as a redox processes, in which one or two valence electrons are accepted by the host. From a chemical point of view, the intercalation process may be described as a reversible topotactic reaction mediated by cation–electron transfer [4]. This process may be schematically represented as



where [Z] represents the lattice with available sites and A represents the host. The electronic structure of the host becomes then the determining factor of the intercalation.

The experimental data concerning the intercalation of lithium in different transition metal dichalcogenides MX<sub>2</sub> (M = Ti, Nb, Mo, Ta; X = S, Se, Te) include the Knight shift in NMR <sup>7</sup>Li studies in the Li<sub>x</sub>-TiS<sub>2</sub> system [6, 7]. It has been observed that the NMR frequency of Li changes from 240 ppm in the metallic state to 12 ppm when it is intercalated in the material. Changes in the f.e.m., as well as an increase of the *c*-axis and the enhancement of the quadrupolar coupling, have also been reported [7–9]. On the other hand, Mössbauer studies of Li-TaS<sub>2</sub> [10] and transmission spectra for the series MX<sub>2</sub> for the transition metal groups IVB, VB and VIB reveal a charge transfer from Li to the CB of

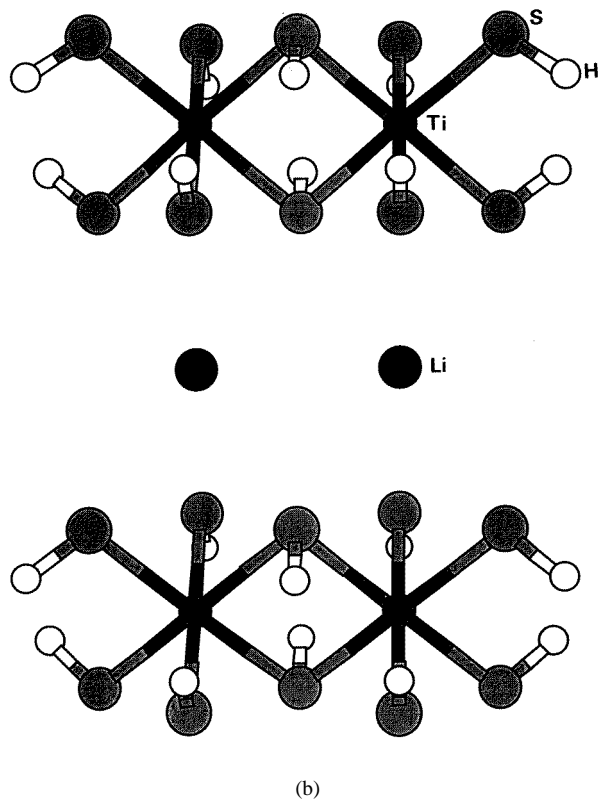


**Figure 1.** The structure of the (a) minimal and (b) extended molecular models.

the material [11, 12]. This charge transfer is not complete, but  $\simeq 10\%$ – $20\%$  of the electronic density of the  $2s$  atomic orbital of Li is retained. On the basis of these results, it has been postulated that Li presents a slightly metallic character.

From a theoretical point of view, the current method used to describe the electronic structure of the intercalated dichalcogenides is the rigid-band (RB) model [13–15]. In this approach, it is assumed that the band structure of the solid remains unchanged upon intercalation. This is based on the fact that the external electronic levels of Li ( $2s$ ) are located several electron volts above the Fermi level of the host lattice: the charge transfer is then driven by the difference in the electronic chemical potential. The charge transfer involves the  $2s$  atomic orbital of Li and the  $(n - 1)d$  valence orbital of the transition metal [16]. After the electron transfer is completed, the electronic chemical potentials equalize at lower energies. In other words, the electrons transferred to the solid fill the electronic bands in such a way that the global electronic chemical potential diminishes.

There is however some evidence against the RB approximation. Self-consistent-field (SCF) band calculations reported by Umrigar *et al* [17] for the  $\text{LiTiS}_2$  system showed that despite the fact that the forms of the electronic bands were maintained, they appeared shifted  $\sim 1$  eV towards more stable energies upon intercalation. Such a change was explained on the basis of the charge redistribution induced by the impurity's local environment. This argument is in agreement with Friedel's screened impurity model [18].



**Figure 1.** (Continued)

Our proposal is that lithium donates its 2s electron to the CB of the solid. The remaining Li<sup>+</sup> ion polarizes its local environment, mainly composed of the coordinating sulphur atoms. This polarization entails a recuperation of a fraction of electron density by Li<sup>+</sup> from the vicinal sulphur atoms, in a process similar to the so-called *back-donation* mechanism proposed in coordination chemistry [19]. It is evident that such a detailed population analysis cannot be performed within a band-type calculation. The methods of quantum chemistry are more suitable for this purpose. In this article we present a quantum chemical approach for analysing the electronic structure of 1T-TiS<sub>2</sub> intercalated with Li. We use a cluster model to simulate the solid, which is derived from a physical model reported elsewhere [20]. Electronic chemical descriptors such as the electronic chemical potential and bond order, and the density of states are used to discuss bonding properties and the migration of Li within the lattice.

## 2. The model and calculations

The methods of quantum chemistry (molecular orbital (MO) theory and density functional theory (DFT)) are useful tools for discussing the electronic structure of solids beyond the RB approximation. This is possible because most of the fundamental changes are mainly induced by local perturbations in the vicinity of the impurity. This specific host-guest interactions are better described by quantum chemical (QC) methods. However, the

major disadvantage of the QC methods is that they require the determination of a minimal molecular model that is able to correctly describe the local interactions, while retaining the major features of the electronic structure of the solid, arising from its periodical properties. We have recently shown that it is possible to derive such a molecular model, using as a physical criterion the invariance of the electronic chemical potential  $\mu$  upon addition of basic (cell) units used to build up the cluster [20, 21]. The electronic chemical potential is a well defined quantity in DFT. It corresponds to the Fermi level in the limit  $T \rightarrow 0$ . It is also related to a relevant physical observable: the work function [22]. Also, by its own definition—the derivative of the electronic energy with respect to the total number of electrons in the system at constant external potential—it becomes the natural physical quantity to discuss when considering the amount and direction of an electron-transfer process.

In DFT, the electronic chemical potential is approximated using a finite-difference formula as follows [23–25]:

$$\mu = \left[ \frac{\partial E}{\partial N} \right]_{v(r)} \cong -\frac{(I + A)}{2} \quad (2)$$

where  $E$  is the electronic energy,  $N$  the total number of electrons and  $v(r)$  the external potential due to the interaction of electrons with the positive compensating charges in the system. From a plot of  $E$  versus  $N$ , it is possible to obtain an approximate derivative by comparing the energy changes from  $N$  to  $N - 1$  and from  $N$  to  $N + 1$  electrons in the system, thereby introducing the ionization potential  $I$  and the electron affinity  $A$ , respectively. There are several ways to estimate the quantity  $\mu$ . The first one is that of simply using experimental values for  $I$  and  $A$ . However, when we are dealing with a molecular model, these quantities are in general not available from experiment. In such a case,  $I$  and  $A$  may be estimated theoretically by: (i) using Slater's electronic transition state concept [26], which has been generalized in DFT by Janak [27], or (ii) using Koopman's theorem [28], which allows one to express these quantities in terms of the frontier one-electron orbital energies of the highest occupied molecular orbital (HOMO)  $\varepsilon_H$  and the lowest unoccupied molecular orbital (LUMO)  $\varepsilon_L$ :

$$\mu \cong \frac{\varepsilon_H + \varepsilon_L}{2}. \quad (3)$$

In this work, equation (3) was used to evaluate  $\mu$ . It has been shown that the electronic chemical potential as defined in equation (2) equals the negative of Pauling's electronegativity  $\chi$  [23, 24]. Both quantities are related by the common property of reaching a constant equilibrium value after two interacting systems exchange electrons to form a stable complex. In the present case, we consider the lattice model having an *intrinsic* electronic chemical potential  $\mu_M$  and the lithium atom having a different chemical potential  $\mu_{Li}$  before they are allowed to interact. Once the intercalation has taken place, a unique equilibrium electronic chemical potential  $\mu_{eq}$  will characterize the intercalated material. The amount and direction of the charge transfer may then be assessed by comparing the density of states (DOS) of the material before and after intercalation.

The molecular model used in the present work was constructed by considering the available structural data obtained from x-ray diffraction studies [1, 29]. For instance, it is well known that Li in 1T-TiS<sub>2</sub> is located at the octahedral (O<sub>h</sub>) sites in the interlaminar VDW region. It has also been observed that upon intercalation, an expansion of the crystallographic *c*-axis of about 0.5 Å occurs, without modification of the O<sub>h</sub> coordination of Ti, and without significant changes in the Ti–S bond lengths. The complete experimental structural parameters used as input to construct the molecular models are summarized in table 1.

**Table 1.** Crystallographic data for the 1T-TiS<sub>2</sub> model.

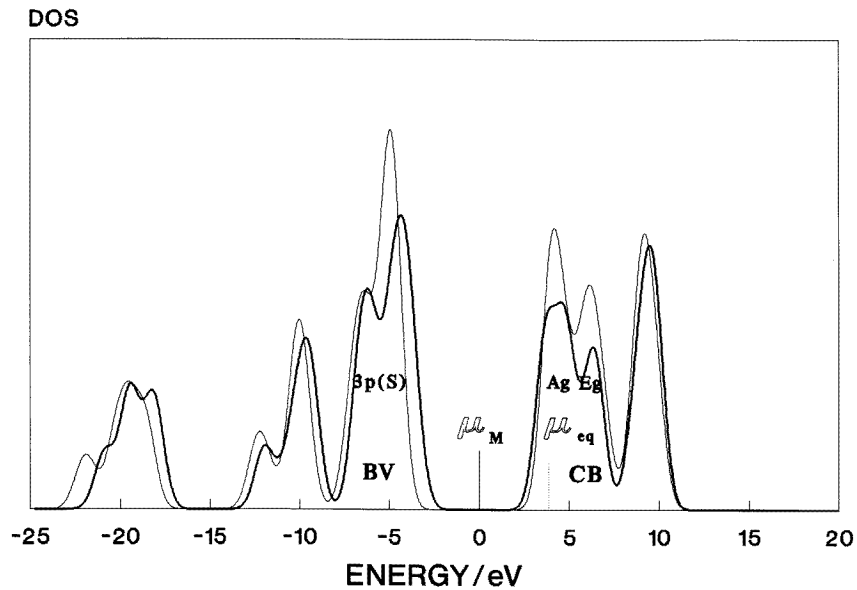
Crystallographic data (Å)	TiS <sub>2</sub>	LiTiS <sub>2</sub>
<i>a</i>	3.41	3.43
<i>c</i>	5.69	6.18
Ti–Ti distance	3.41	3.43
Ti–S distance	2.40	2.44
S–S distance	3.41	3.43
S–S distance in the plane	3.41	3.43
S–S distance across the VDW gap	3.51	3.90
Li–Ti distance between the VDW gap		3.09
Li–S distance		2.60

The basic unit is then composed of a hexagonal unit cell, corresponding to a [TiS<sub>6</sub>H<sub>6</sub>]<sup>2-</sup> structure. The added hydrogen atoms are introduced with the twofold purpose of reducing the high global charge of the model system, and—mainly—to saturate the *dangling* orbitals of sulphur at the boundary of the model. These unsaturated orbitals may lead to the creation of fictitious electronic states in the band structure. The location of the hydrogen atoms is determined by a full geometry optimization of the unit cell. The INDO/1 semiempirical method, specially parametrized for transition metal compounds, was used in the geometry-optimization procedure. The resulting length of the Ti–S bond was 1.39 Å and the internal S–Ti–S bond angles were very close to the experimental geometry. From this unit cell, we define two molecular models: [Ti<sub>2</sub>S<sub>12</sub>H<sub>12</sub>]<sup>4-</sup> (figure 1(a)), and [Ti<sub>4</sub>S<sub>20</sub>H<sub>20</sub>]<sup>4-</sup> (figure 1(b)). In these structures, the interlaminal VDW space and a (distorted) O<sub>h</sub> symmetry around the Ti atoms is maintained. Both models, figures 1(a) and 1(b), correspond to molecular structures optimized at the INDO/1 level.

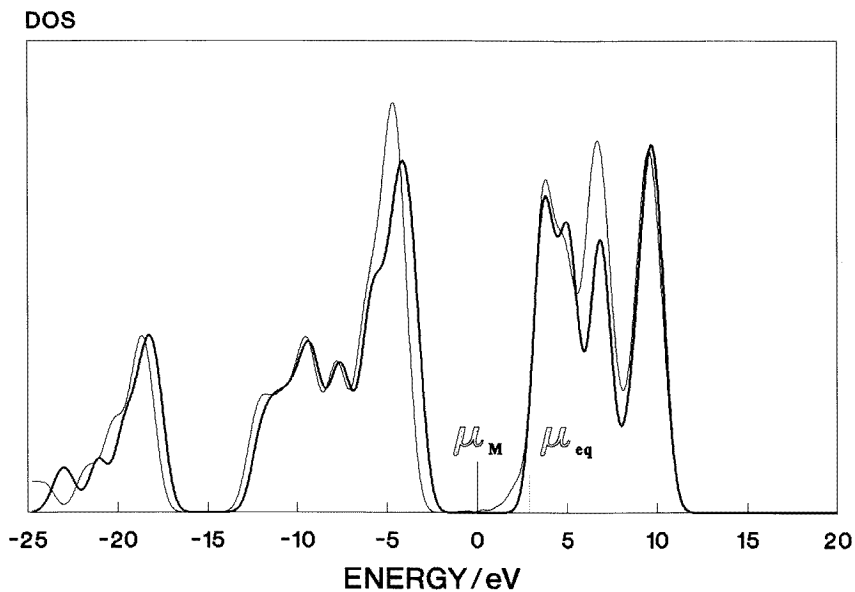
The electronic structure calculations were performed using the semiempirical HF-INDO/1 [30, 31] method on the models of figures 1(a) and 1(b) using a valence electron basis set. Additional HF Slater Amsterdam density functional (ADF) [32, 33] code was applied to the minimal structure of figure 1(a) with the sole purpose of checking that the semiempirical calculation provides reliable electronic structures. This latter approach solves the Kohn–Sham self-consistent equations within the local density approximation (LDA) with gradient corrections for the exchange and correlation potentials. In the ADF calculations, the LDA exchange–correlation potential suggested by Vosko and Wilk [34] was used. The non-local gradient correction for exchange proposed by Becke [35] and the non-local correction for correlation proposed by Perdew [36] were used. Finally, the DOS was approached via a Gaussian distribution of the one-electron eigenstates obtained by the QC methods described above, and considering a band width of 0.5 eV [37].

### 3. Results and discussion

The DOS depicted in figures 2 and 3 were obtained through INDO/1 calculations performed on the models of figures 1(a) and 1(b), respectively. The VB presents a dominant 3p sulphur character, whereas the CB is mostly composed of the 3d atomic orbitals of Ti of symmetry T<sub>2g</sub>. The electronic chemical potential shift ( $\Delta\mu = \mu_{eq} - \mu_M > 0$ ) after and before intercalation reveals a charge transfer from the impurity to the CB of the material:  $\mu_{eq} > \mu_M$  indicates that electrons (or fractions of electrons) flowed from Li towards the CB of the chalcogenide. The DOS shown in figure 4, corresponding to an ADF calculation

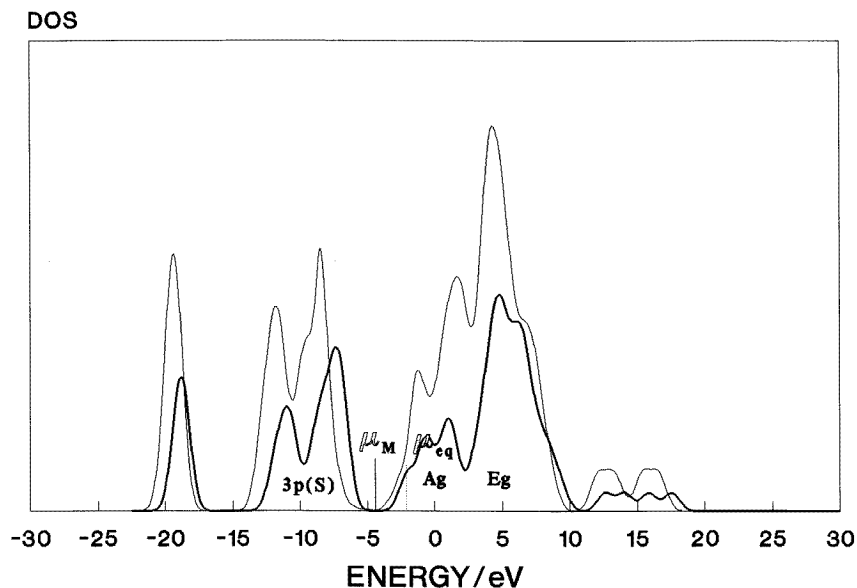


**Figure 2.** The density of states (DOS) for the minimal structure of figure 1(a) with (solid line) and without (bold line) lithium. An INDO/1 calculation.



**Figure 3.** The density of states (DOS) for the extended structure of figure 1(b) with (solid line) and without (bold line) lithium. An INDO/1 calculation.

performed on the minimal structure of figure 1(a), confirms the charge-transfer pattern obtained at the INDO/1 level. Comparison of the DOS in the presence and in the absence of Li also shows the shifting of the energy bands toward lower energies, especially the 3p



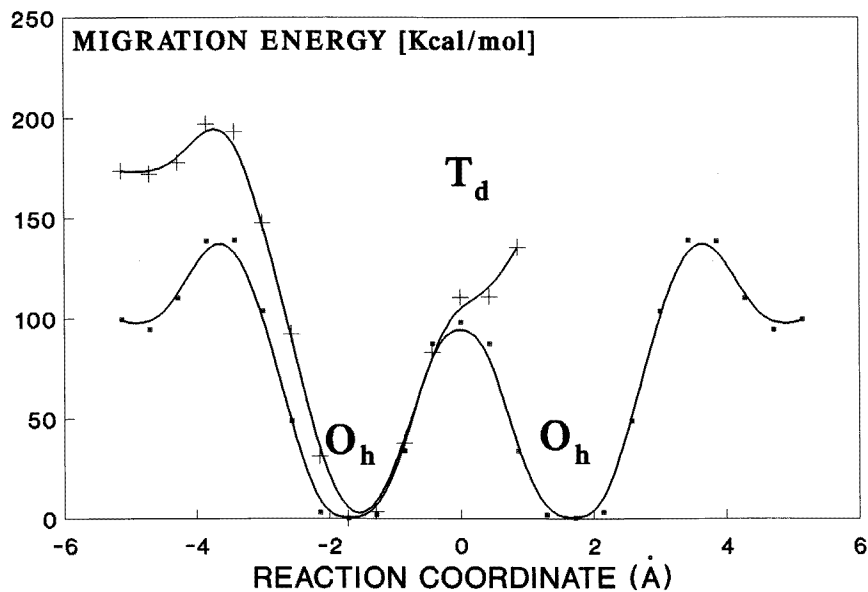
**Figure 4.** The density of states (DOS) for the minimal structure of figure 1(a) with (solid line) and without (bold line) lithium. An ADF calculation (see the text).

sulphur VB.

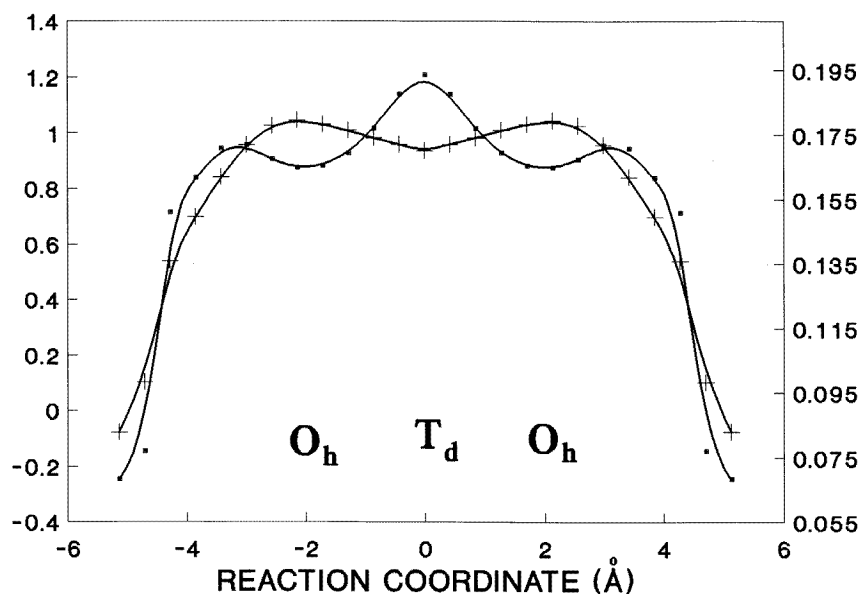
A Mulliken population analysis shows an increase of the electron density at the 3d<sub>z<sup>2</sup></sub> orbital of Ti, whereas the sulphur atoms located towards the interlaminar VDW region diminish the orbitals' electronic population. Since the electronic chemical potential of Li is located several eV above the Fermi level of the isolated lattice, we propose that there may be a complete transfer of the 2s electron of Li, as predicted by the RB model [16], leaving a Li<sup>+</sup> ion in the VDW gap. However, the presence of the positively charged impurity may then induce an electronic polarization on the vicinal sulphur atoms which donates back a fraction of the electron density to Li<sup>+</sup>, in a process similar to that observed in the coordination chemistry compounds [19]. The predicted Li ionicity (75%) compares well with that observed in NMR experiments (80%) [7]. Previous calculations for TiS<sub>2</sub> and LiTiS<sub>2</sub> by Umrigar *et al* [17], using a self-consistent linearized augmented-plane-wave (LAPW) scheme, showed that the occupied levels did not present a dominant Li character. Furthermore, the additional charge of the Li electron was found to be spread out in the region between Li and S, reinforcing our hypothesis of the electronic polarization induced in the sulphur environment by the Li<sup>+</sup> ion. It seems, then, that the electronic polarization of the sulphur atoms in the VDW gap, described in our chemical model as a *back-donation* process, corresponds to the screened impurity effect of Friedel's model [18].

Another way to search for evidence of the electronic polarization in the coordinating sulphur environment is to analyse the Li migration potential profiles (MPP). We assume that Li atoms may migrate within the lattice, along a hypothetical path defined in the midplane of the VDW gap. At each point of this path, we evaluate both the Li ionicity and the bond orders between Li and the sulphur atoms in the local environment. INDO/1 calculations of MPP for the model of figure 1(b) are shown in figure 5. The MPP shows a double-well profile; each well is located at an O<sub>h</sub> site and the wells are separated by a potential barrier at





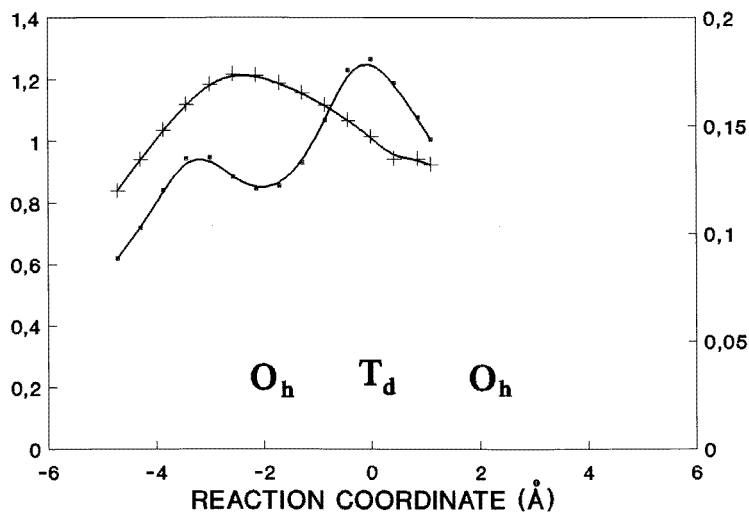
**Figure 5.** The migration potential profile (MPP) for a lithium atom (■) in the extended structure and for a second lithium atom (+) in the presence of a lithium atom at the  $O_h$  site. An INDO/1 calculation.



**Figure 6.** The variation of the net charge of Li (■) and the Li-S bond order (+) during the migration of a lithium atom within the extended structure of figure 1(b). An INDO/1 calculation.

the tetrahedral ( $T_h$ ) site. The barrier shown in the long-range regime may be meaningless, because it may correspond to the repulsion between Li and the hydrogen atoms used to

saturate the dangling orbitals at the boundary of the models. However, the analysis of the MPP for the model of figure 1(b) together with the variation of the bond order and Li ionicity *within* the lattice (figure 6) *is* meaningful. For instance, at the minima of the MPP, the ionicity of Li is a minimum but the bond order is a maximum. On the other hand, at the T<sub>h</sub> site, which is energetically unfavourable, the situation is completely reversed: the Li ionicity becomes a maximum whereas the bond order displays a minimum. These results indicate that Li intercalated in 1T-TiS<sub>2</sub> presents its lower oxidation state at the O<sub>h</sub> site. At this site, the interaction with the sulphur environment is at a maximum, and therefore the bonding properties of Li within the layer also reinforce our proposal of a back-donation effect in the Li-S bond.



**Figure 7.** The variation of the net charge (■) and the Li-S bond order (+) during the migration of a second lithium atom, in the presence of a Li atom trapped at the O<sub>h</sub> site. An INDO/1 calculation on the model.

The proposed model is also useful for analysing the effect of the intercalation of a second Li atom, in the presence of a first Li atom fixed at one of the O<sub>h</sub> sites in the lattice. The corresponding ionicity curve is shown in figure 7. It may be observed that despite the fact that the form of the ionicity curve is conserved as our hypothetical migration coordinate is varied, the ionicity displayed by the second Li atom is lower than that corresponding to the migration of the first Li impurity. This effect may be of some interest if we consider for instance the charge capacity of the intercalated lattice as a function of the fraction of Li intercalated. The results obtained here suggest that the charge transfer between the second Li and the lattice is lower than that corresponding to a material free of impurities. This effect may be explained within our molecular model as follows: the electronegativity of any system may be considered as a function of the charge acquired by the system, from a neutral reference state [38, 39]. Up to first order it is given by

$$\chi(Q) = \chi(Q) + Q \left. \frac{\partial \chi}{\partial Q} \right|_{Q=0} . \quad (4)$$

The first term of equation (4) represents in this case the *intrinsic* electronegativity of the lattice (i.e. the electronegativity in the absence of the impurity). The ionicity of the second

Li atom intercalated in our model is then driven by the second term of equation (4). It seems that after the intercalation of the first Li atom, the electronegativity of the doped lattice drops from its *intrinsic*  $\chi^0$  to the actual  $\chi(Q)$  value. The amount of electron transfer from Li to the CB of the doped material is expected to decrease, as predicted by equation (4), by an amount proportional to the second term.

#### 4. Concluding remarks

We have presented a molecular model to allow us to discuss the electronic structure and bonding properties of Li intercalated in 1T-TiS<sub>2</sub>. The present approach focuses mainly on the local host–guest interactions, modelled through a quantum chemical framework. The electronic chemical potential concept appears as a useful electronic indicator for discussing charge transfer in these systems, beyond the RB model. The relevance of local interactions involving the close impurity's environment allows us to correctly explain the slight metallic character observed for Li intercalated in these materials. The calculated ionicity of Li within the lattice is in good agreement with the experimental data and with previous theoretical calculations performed at a different level of the theory [17]. The fraction of electron density retained by Li in this system may be explained by an electronic polarization effect induced in the coordinating sulphur atoms, in a process similar to the back-donation mechanism proposed in the chemistry of coordination compounds. The QM approach is also useful for discussing bonding and migration properties in these systems.

#### Acknowledgment

This work was supported by FONDECYT under contracts 2940003 and 1940348.

#### References

- [1] Friend R H and Yoffe A D 1987 *Adv. Phys.* **36** 1  
Yoffe A D 1990 *Solid State Ion.* **39** 1
- [2] Dines M B 1978 *Inorg. Chem.* **17** 763  
Dines M B 1978 *Mater. Res. Bull.* **10** 287
- [3] Gerhards A, Roede H and Wiegers G 1983 *Synth. Met.* **10** 51
- [4] Schollhor R 1980 *Angew. Chem. Int. Edn Engl.* **19** 983
- [5] Mackinnon W R 1992 *Chemical Physics of Intercalations (NATO ASI series B, vol 172)* ed A P Legrand (New York: Plenum)
- [6] Balkanski M 1991 *Phys. Scr. T* **39** 9  
Schollhorn R 1990 *Solid State Ion.* **39** 23  
Yoffe A D 1983 *Solid State Ion.* **9+10** 59
- [7] Silbernagel B and Whittingham M S 1976 *J. Chem. Phys.* **64** 3670  
Silbernagel B 1975 *Solid State Commun.* **17** 361
- [8] Dahn J, Mackinnon W R and Haering R 1982 *Can. J. Phys.* **58** 207
- [9] Julien C and Samaras Y 1992 *Phys. Rev. B* **45** 13 390
- [10] Butz T and Lerf A 1986 *Ber. Bunsenges. Phys. Chem.* **90** 638
- [11] Beal A and Nulsen S 1981 *Phil. Mag.* B **42** 965
- [12] Beal A and Nulsen S 1981 *Phil. Mag.* B **43** 985
- [13] Whittingham M S 1978 *Prog. Solid State Chem.* **12** 41
- [14] Friend R H and Yoffe A D 1969 *Adv. Phys.* **18** 193  
Huisman H and Haas C 1971 *J. Solid State Chem.* **3** 56  
de Groot R and Haas C 1975 *Solid State Commun.* **17** 887
- [15] Liang W Y 1989 *Mater. Sci. Eng. B* **3** 139

- [16] Liang W Y 1990 *Intercalation in Layered Materials (NATO ASI series B, vol 148)* ed M S Dresselhaus (New York: Plenum) p 31
- [17] Umrigar C, Ellis D, Wang D, Krakauer H and Posternak M 1982 *Phys. Rev. B* **26** 4935
- [18] Friedel J 1954 *Adv. Phys.* **3** 446
- [19] Brec R and Rouxel J 1990 *Intercalation in Layered Materials (NATO ASI series B, vol 148)* ed M S Dresselhaus (New York: Plenum) p 75
- [20] Mendizábal F, Contreras R and Aizman A 1995 *J. Mol. Struct. (TheoChem)* **335** 161
- [21] Mendizábal F, Contreras R and Aizman A 1994 *Int. J. Quantum Chem.* **56** 819
- [22] Ashcroft N W and Mermin N D 1978 *Solid State Physics* (New York: Holt, Rinehart and Winston)
- [23] Parr R G and Yang W 1989 *Density-Functional Theory of Atoms and Molecules* (Oxford: Oxford University Press)
- [24] Parr R G, Donnelly R, Levy M and Palke E 1978 *J. Chem. Phys.* **68** 3801
- [25] Pearson R G 1993 *Accounts Chem. Res.* **26** 250
- [26] Slater J C 1974 *The Self-Consistent Field For Molecules and Solids: Quantum Theory of Molecules and Solids* vol 4 (New York: McGraw-Hill)
- [27] Janak J F 1978 *Phys. Rev. B* **18** 7165
- [28] Koopman T A 1933 *Physica* **1** 104
- [29] Dahn J, Py M and Haering R 1982 *Can. J. Phys.* **60** 307
- [30] Bacon A and Zerner M 1979 *Theor. Chim. Acta* **53** 21
- [31] Zerner M, Loew G and Kirchner R 1980 *J. Am. Chem. Soc.* **102** 589
- [32] Baerends E, Ellis D and Ros P 1973 *Chem. Phys.* **2** 41
- [33] Baerends E and Ros P 1978 *Int. J. Quantum Chem. Symp.* **12** 169
- [34] Vosko S H and Wilk L 1983 *J. Phys. B: At. Mol. Phys.* **16** 3687
- [35] Becke A D 1988 *J. Chem. Phys.* **88** 1053
- [36] Perdew J P 1986 *Phys. Rev. B* **33** 8822
- [37] Yu H L 1977 *Phys. Rev. B* **15** 3609
- [38] Huheey J E 1971 *J. Org. Chem.* **36** 204
- [39] Politzer P 1987 *J. Chem. Phys.* **86** 1072