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# The electronic chemical potential as a basis for a cluster model approximation for intercalation of Li in $1T - \text{TiS}_2$ <sup>☆</sup>

F. Mendizabal<sup>a,\*</sup>, R. Contreras<sup>a</sup>, A. Aizman<sup>b</sup><sup>a</sup>Departamento de Química, Centro de Mecánica Cuántica Aplicada, Fac. de Ciencias, Universidad de Chile, Casilla 653-Santiago, Chile<sup>b</sup>Fac. de Ciencia, Universidad Técnica F. Santa María, Casilla 110-V, Valparaíso, Chile

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## Abstract

The representation of the electronic structure of intercalated  $1T - \text{TiS}_2$  with lithium by a *cluster* approximation is discussed. The electronic chemical potential, defined in the context of density functional theory, is used as a criterion to determine the minimal units that retain the major electronic properties of the actual solid. The results indicate that a structure containing 3–4 *hexagonal unit cells* of  $\text{TiS}_2$ , with an octahedral coordination around the transition metal, is good enough to reproduce the major features of the electronic structure of the infinite layered solid. Analysis of the valence and conducting bands shows good qualitative agreement with band theory calculations. A partial electron transfer from Li to the lattice is predicted, in good agreement with experimental NMR data for this system.

## 1. Introduction

Intercalation chemistry has received a great deal of attention from experimental and theoretical points of view. These compounds display electronic and optical properties with potential application in material sciences, especially in the field of superconductors and batteries. Attention is at present focused on the chemistry of metal transition dichalcogenides, which present a layered structure, separated by interlaminar spaces called van der Waals (VDW) gap, where atoms and molecules may be intercalated [1,2]. This property is very interesting since it allows the study of chemical reactivity in an environment quite different from that observed in the liquid state.

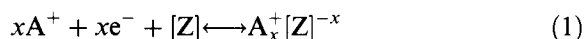
The intercalation process is generally associated with an electron transfer from the guest (usually alkali and transition metal atoms or Lewis base like molecules) to the host lattice (in general, transition metal dichalcogenides). A secondary structural effect usually observed is the expansion of the VDW gap.

The presence of the impurity in the lattice is essentially responsible for the change of the optical and electronic properties of the material. The electrons transferred from the guest are incorporated into the conduction band of the solid. At the same time, the electronic structure of the impurity is influenced by the rigid environment, changing its potential reactivity pattern. A large amount of experimental data has been accumulated and the development of microscopic models to rationalize the available information will be crucial in predicting properties of new materials [3,4].

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\* Corresponding author.

From a chemical point of view, the intercalation process is a reversible topotactic redox reaction by electron-ion transfer [1,2]. A particular class of reaction is the electron-cation transfer:



where  $[Z]$  represents the lattice with available sites and  $A$  represents the guest.

The theoretical models that explain the intercalation processes in these materials are mainly based on band theory calculations [5], in the rigid band approximation. This approach assumes that the conduction band is mainly composed of the d orbitals of the transition metal of the host, whereas the valence band is formed by the p orbitals of the chalcogenide (sulfide or selenide) [6]. Within this model, a complete electron transfer (one electron per guest) is assumed. There is some experimental evidence, however, that fractional electron transfer may be involved in this process. Furthermore, specific guest-host interaction, bonding and ionic diffusion cannot be discussed within the rigid band approach. The fact that fractional electron transfer could be present in intercalation reactions should be reflected in the actual oxidation number of the transition metal (TM) of the lattice [7]. However, the method of quantum chemistry (molecular orbital (MO) and density functional theories) may be helpful to discuss this problem beyond the RB approximation. In spite of the success of the band theory to describe the long-range periodic interactions of the solids, the major part of the electronic structure of the lattice is determined by a local environment formed by a reduced arrangement of atoms [8]. This specific interaction is best described within the MO theory [9]. The major problem here is the determination of a *minimal* molecular structure (*cluster* model) that describes the local interactions correctly, while retaining the major features of the electronic structure of the solid coming from its periodical properties [10].

In this work we propose a *cluster* like model, based on the electronic chemical potential concept of density functional theory (DFT), to discuss the change of the electronic structure of  $1T - \text{TiS}_2$  upon intercalation with Li.

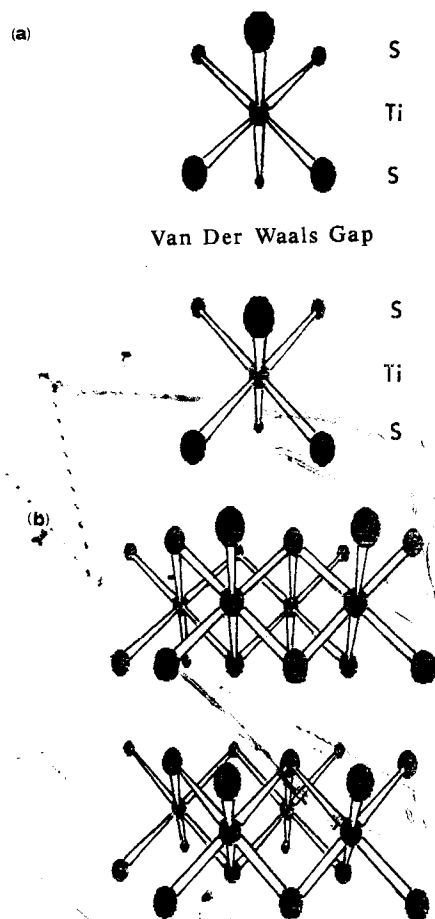


Fig. 1. Cluster model for  $1T - \text{TiS}_2$ : (a) basic unit composed of two hexagonal unit cells and (b) cluster model composed of four basic units ( $\text{Ti}_8\text{S}_{32}$ ).

## 2. Model and calculations

The Fermi level is a reference state separating the occupied and unoccupied electronic levels in a solid. Within a microscopic model of the system, the Fermi level may be represented as the electronic chemical potential  $\mu$  [11]. This basic quantity is defined, in the context of DFT as [12]

$$\mu = \left( \frac{\partial E}{\partial N} \right)_v \approx -\frac{I + A}{2} \quad (2)$$

where  $E$  is the electronic energy,  $N$  the number of electrons,  $v$  the external potential,  $I$  the ionization potential and  $A$  the electron affinity. Working definitions of the quantities  $I$  and  $A$  are possible within

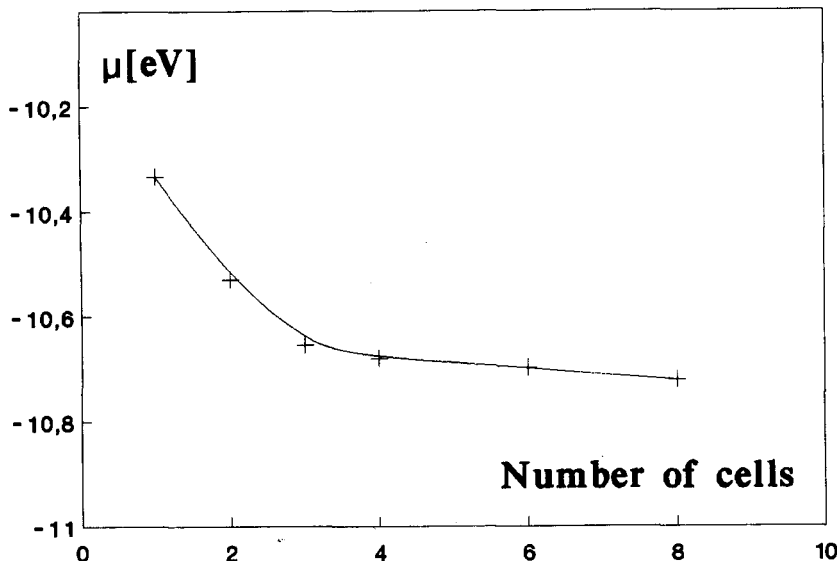


Fig. 2. Variation of the electronic chemical potential with increasing cluster size.

MO theory [13]. For instance, by using Koopmans theorem [14], the ionization potential and electron affinity may be approximated as  $I = -\epsilon_{\text{HOMO}}$  and  $A = -\epsilon_{\text{LUMO}}$ , respectively. With these approximations, the electronic chemical potential becomes

$$\mu = \frac{\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}}}{2} \quad (3)$$

The use of standard quantum chemical methods to simulate a solid by means of a finite-size cluster has the problem that the electronic properties present an oscillating behavior with increasing cluster size [10]. This feature greatly diminishes the reliability and confidence of the results obtained by this procedure. For this reason, it is desirable to have a physical criterion to establish a *minimal* cluster size for which the relevant electronic properties reach a stable regime upon increasing the number of unit cells. Being the intercalation, an electron transfer reaction, a natural property to describe this process, is the electronic chemical potential. Then we make the ansatz that the minimal cluster structure corresponds to the one where the electronic chemical potential remains approximately unchanged upon increasing the cluster size. In this way the  $\mu$  value associated with the minimal structure will describe reasonably well the electronic chemical potential of the solid.

Calculations for different clusters were performed using the extended Hückel MO code. The basic unit composed of two hexagonal unit cells shown in Fig. 1(a) was considered. This unit considers a VDW gap to mimic the interlaminar spacing and keeps the right octahedral symmetry around the Ti atoms. Bigger clusters are built by adding successive units, maintaining the octahedral symmetry. Intercalated Li atoms are placed in octahedral sites formed by the sulfur bilayers in line with the Ti atoms. For each cluster the electronic chemical potential was obtained through Eq. (3).

### 3. Results and discussion

Fig. 2 displays the results obtained for the electronic chemical potential variation with increasing cluster size. It may be seen that for a four-unit structure,  $\mu$  reaches a critical value that remains almost constant upon addition of new basic units. Then, the representative cluster corresponds to  $\text{Ti}_8\text{S}_{32}$ , displayed in Fig. 1(b). The Ti atom is taken in its  $d^0$  configuration.

In Fig. 3 the electronic structure of the hexagonal unit cell and the cluster model are compared with the band structure obtained from a semiempirical

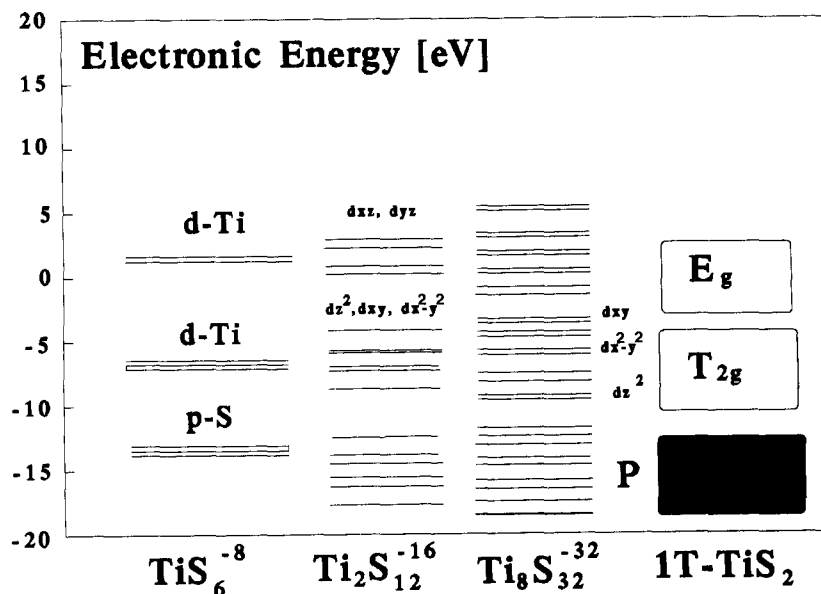


Fig. 3. Comparison between the electronic structure of different cluster models and the density of state distribution for  $1\text{T-TiS}_2$  from Ref. [15].

tight-binding method reported by McCanny [15]. The band analysis shows that the valence band is mostly formed by the p orbitals of the sulfur atoms. The conducting band is mostly formed by the  $d_{z^2}d_{x^2-y^2}$  and  $d_{yx}$  orbitals of  $T_{2g}$  symmetry, of the TM atom. A third band of  $E_g$  symmetry and formed by  $d_{yz}$  and  $d_{xz}$  orbitals is also reported in Ref. [15]. The  $T_{2g}$  band is proposed to have non-bonding character, whereas the  $E_g$  band displays an antibonding character. Furthermore, due to symmetry factors, the distortion of the octahedral hexagonal cell entails the  $d_{z^2}$  orbitals to be observed at the bottom of the  $T_{2g}$  band [15].

Our  $\text{Ti}_8\text{S}_{32}$  cluster model presents the same pattern in the components of the all three bands reported by McCanny. Furthermore, orbitals showing a strong  $d_{z^2}$  character lie at the bottom of the d-band structure of our model cluster, resembling the results obtained in the tight binding calculation.

Our derived cluster model was used to study the intercalation of Li in the  $1\text{T-TiS}_2$  lattice. Firstly we became interested in the analysis of the variation of the electronic chemical potential upon successive intercalations of Li in the available octahedral site. A correction for the VDW gap

expansion was included by increasing it to 0.5 Å which corresponds to the experimentally observed expansion [16]. Fig. 4 summarizes the result obtained. It may be observed that after the intercalation of one Li atom, the chemical potential reaches a value that remains approximately constant upon intercalation of more Li atoms. This result may be interpreted in terms of the absolute electronegativity changes of the lattice upon successive additions of Li. This is a valid approach since within the scheme of DFT the absolute electronegativity  $\chi$  corresponds to the negative of the chemical potential. A useful model to discuss the electronegativity changes was proposed by Politzer [17]. In this model, the electronegativity of any system is considered as a function of the charge  $Q$  acquired by the system, from a neutral reference state. Up to first order, the function  $\chi(Q)$  is given by

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

where the first term of Eq. (4) represents in this case the electronegativity of the lattice in the absence of Li (intrinsic electronegativity). In other words, after addition of the first Li atom, the variation

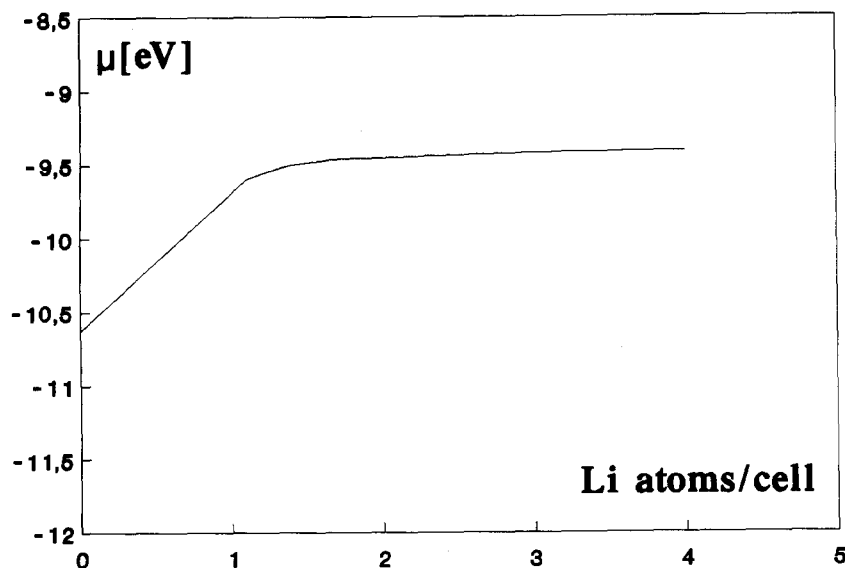


Fig. 4. Variation of the electronic chemical potential of the cluster model with successive intercalation of Li.

of the electronegativity given by the second term of Eq. (4) causes the electronegativity of the doped system to diminish dramatically to a constant *equilibrium* value, causing a decrease in the tendency of acquiring more charge. This result is consistent with NMR experimental results showing that as the intercalation proceeds, the electron donation becomes progressively less complete [16]. In fact our model predicts an average Li ionicity of about 75%. However, the electron density around Sulfur atoms decreases upon successive intercalation of Li: it seems possible then that in a first step, Li donates charge to the Ti atoms and a fraction of electronic charge is recovered via polarization of the sulfur atoms around it. This explanation is consistent with band structure calculations on these systems [18].

#### 4. Concluding remarks

A cluster like approach for the study of intercalation of Li in the  $1T - \text{TiS}_2$  system has been presented. The choice of the minimal molecular unity to represent the layered dichalcogenide was performed on the basis of the variation of the electronic chemical potential upon addition of

hexagonal unit cells into the system. Our calculations show that for a cluster composed of four units, the electronic chemical potential is stabilized around an almost constant value. The electronic structure of the model system reproduces qualitatively well the relevant aspects of the band structure of the solid obtained from a tight-binding calculation. The model cluster was used to study intercalation of Li in this system. The following relevant results were obtained.

(i) The intercalation of Li into the  $1T - \text{TiS}_2$  lattice may be analyzed as an electron transfer reaction. Within this model, the process may be discussed in terms of the variation of the electronegativity of the system upon successive intercalations with Li. The results obtained show that after intercalation of the first Li atom, the electronic chemical potential (i.e. the negative of the electronegativity) increases rapidly as the lattice gains negative charge, and correspondingly diminishes its tendency to acquire more. This result is completely consistent with experimental observation obtained from NMR studies which show that as the intercalation proceeds, the electron donation becomes progressively less complete [16].

(ii) Our calculations of Li ionicity are consistent with the above explanation: our model predicts an

average Li ionicity of about 75%, in good agreement with previous calculations on this system [18]. Also, the presence of ionized Li in the lattice induces polarization in the adjacent sulfur atoms, producing a *backdonation*-like effect towards the intercalated Li.

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